Supporting Information

Copper Catalyzed Arylation/C-C Bond Activation: An Approach toward α-Aryl Ketones

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Experimental Details

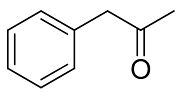
General Information

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point is between 30-60 ^{o}C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they are listed as volume/volume ratios. NMR spectra were recorded on a Varian Mercury spectrometers at 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR), a Varian Mercury spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), or a Varian Mercury spectrometer at 600 MHz (^{1}H NMR), 150 MHz (^{13}C NMR). Tetramethylsilane was used as an internal standard. All ^{1}H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument, accurate masses are reported for the molecular ion ($[M]^{+}$). Selective ratios were recorded with a Varian GC 2000 gas chromatography instrument with a FID detector. And GC yield were determined by the same instrument while naphthalene was used as the internal standard. GC-Ms spectra were recorded on a Varian GC- Ms spectra were recorded on a Varian GC-Ms 3900-2100T. For the ReactIR kinetic experiments, the reaction spectra were recorded using a IC 10 from Mettler-Toledo AutoChem fitted with a diamond-tipped probe. Data manipulation was carried out using the iC IR software, version 1. 05.

Preparation of (pincer thioamide)-CuCl:

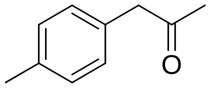
N^1,N^3-dibutylbenzene-1,3-bis(carbothioamide) (8 mmol) was dissolved in CH_3CN to form a yellow solution. While stirring, this solution was added dropwise to the solution of CuCl (5 mmol) in CH_3CN. And the mixture is refluxed during a period of five to six hours, during which time the formation of yellow precipitate. The precipitate was filtered out and washed with CH_3CN three times. The solid was vacuum-dried, and 1.4 g (yield 70%) of a yellow solid was obtained. ^{1}H NMR (300 MHz, d^6-DMSO): δ 10.63 (s, 2H), 7.99 (s, 1H), 7.73-7.70 (d, J = 7.2 Hz, 2H), 7.47-7.42 (t, J = 7.4 Hz, 1H), 3.68-3.64 (t, J = 6.6 Hz, 4H), 1.70-1.61 (m, 4H), 1.41-1.29 (m, 4H), 0.93-0.89 (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, d^6-DMSO): δ 200.55, 145.97, 135.17, 133.73, 132.91, 52.42, 34.87, 25.56, 19.51.

General Procedures for the α-Arylation of Ketone:



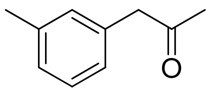
3a

1-Phenylpropan-2-one.[1] A mixture of iodobenzene **1a** (1.0 mmol), acetylacetone **2a** (3.0 mmol), CuI (10 mol %), and $K_3PO_4 \cdot 3H_2O$ (3.0 mmol) in DMSO (3 mL) was stirred in N_2 at 90 ^oC. After completion of the reaction, as indicated by GC, the mixture was quenched with diluted hydrochloride (2 mL, 2M), the solution was extracted with ethyl acetate (3 × 5 mL). The organic layers were combined, and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel to afford **3a** in 75% yield. The spectroscopic data of all the products are presented below. All the known compounds gave satisfactory spectroscopic values and are analogue to spectroscopic data reported in the literature. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.30 (t, J = 7.5 Hz, 2H), 7.26-7.24 (t, J = 7.2 Hz, 1H), 7.20-7.18 (d, J = 7.8 Hz, 2H), 3.67 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.21, 134.09, 129.31, 129.14, 128.64, 128.47, 126.96, 126.77, 50.80, 29.09.



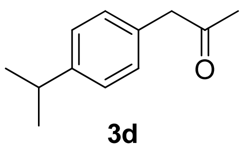
3b

1-*p*-Tolylpropan-2-one.[2] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.14-7.13 (d, *J* = 7.8 Hz, 2H), 7.09-7.07 (d, *J* = 8.4 Hz, 2H), 3.64 (s, 2H), 2.32 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.68, 136.63, 131.16, 129.51, 129.32, 129.20, 129.14, 50.60, 29.15, 21.09.



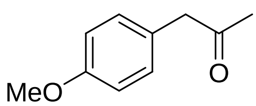
3c

1-*m*-Tolylpropan-2-one.[2] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25-7.21 (q, *J* = 8.8 Hz, 1H), 7.09-7.07 (d, *J* = 7.2 Hz, 1H), 7.02-6.99 (t, *J* = 6.6 Hz, 2H), 3.65 (s, 2H), 2.34 (s, 3H) 2.14 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.57, 138.33, 134.05, 130.11, 129.96, 128.64, 128.49, 127.81, 127.66, 126.39, 126.24, 50.93, 29.17, 21.32.



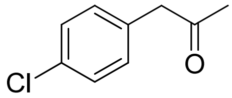
3d

1-Iodo-4-isopropylbenzene.[3] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12-7.03 (m, 4H), 3.57 (s, 2H), 2.85-2.76 (m, 1H), 2.06 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.04, 147.86, 131.70, 129.52, 127.05, 50.85, 33.96, 29.50, 24.20.



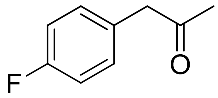
3e

1-(4-Methoxyphenyl)propan-2-one.[1] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11-7.10 (d, *J* = 8.4 Hz, 2H), 6.87-6.85 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 3H), 3.61 (s, 2H), 2.12 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.67, 158.46, 130.30, 130.14, 126.10, 114.02, 113.91, 55.10, 49.86, 28.92.



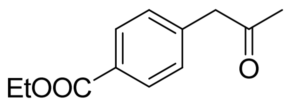
3f

1-(4-Chlorophenyl)propan-2-one.[1] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30-7.29 (d, *J* = 7.8 Hz, 2H), 7.13-7.12 (d, *J* = 7.8 Hz, 2H), 3.67 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 205.59, 132.89, 132.49, 130.76, 130.61, 128.81, 128.66, 49.93, 29.34.



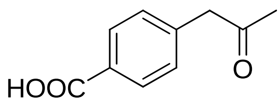
3g

1-(4-Fluorophenyl)propan-2-one.[4] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16-7.14 (t, *J* = 6.0 Hz, 2H), 7.03-7.00 (t, *J* = 7.8 Hz, 2H), 3.67 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 205.95, 162.67, 161.04, 130.96, 130.76, 129.83, 115.60, 115.45, 115.31, 49.77, 29.23.



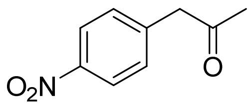
3h

Ethyl 4-(2-oxopropyl)benzoate.[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02-8.01 (d, *J* = 8.4 Hz, 2H), 7.28-7.26 (d, *J* = 8.4 Hz, 2H), 4.39-4.35 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 2H), 2.17 (s, 3H), 1.40-1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 205.14, 166.14, 139.08, 129.72, 129.39, 129.21, 129.12, 60.77, 50.49, 29.34, 14.19.



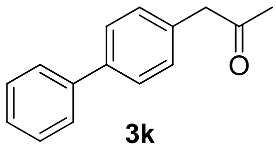
3i

4-(2-Oxopropyl)benzoic acid.[6] ^{1}H NMR (400 MHz, d^6-DMSO): δ 7.86-7.84 (d, *J* = 8.0 Hz, 2H), 7.26-7.24 (d, *J* = 8.0 Hz, 2H), 3.81 (s, 2H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ 205.85, 167.74, 140.55, 130.37, 129.75, 129.55, 49.82, 30.13.



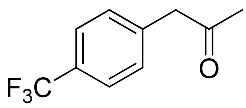
3j

1-(4-Nitrophenyl)propan-2-one.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21-8.19 (d, *J* = 8.4 Hz, 2H), 7.38-7.36 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.40, 141.38, 130.42, 123.69, 115.57, 49.96, 29.81.



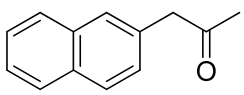
3k

1-(Biphenyl-4-yl)propan-2-one.[8] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58-7.55 (q, *J* = 6.2 Hz, 4H), 7.43-7.41 (t, *J* = 7.8 Hz, 2H), 7.34-7.32 (t, *J* = 7.2 Hz, 1H), 7.26-7.25 (d, *J* = 7.8 Hz, 2H), 3.72 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.25, 140.59, 139.90, 133.14, 129.82, 129.66, 128.76, 128.61, 127.43, 127.31, 126.99, 126.89, 126.57, 50.48, 29.33, 29.29.



3l

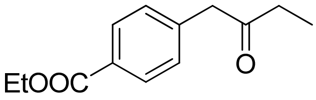
1-(4-(Trifluoromethyl)phenyl)propan-2-one.[7] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60-7.59 (d, *J* = 7.8 Hz, 2H), 7.32-7.31 (d, *J* = 7.8 Hz, 2H), 3.78 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 205.13, 138.00, 129.87, 129.71, 129.46, 129.25, 125.61, 125.49, 124.97, 123.17, 50.32, 29.61.



3m

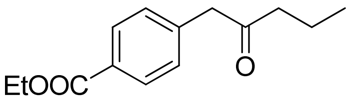
1-(Naphthalen-2-yl)propan-2-one.[6] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81-7.78 (q, *J* = 7.4 Hz, 3H), 7.65 (s, 1H), 7.48-7.43 (m, 2H), 7.31-7.29 (d, *J* = 8.4 Hz, 1H), 3.82 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.36, 133.43, 132.31, 131.66, 128.31, 128.06, 127.97, 127.57, 127.48, 127.40, 127.24, 126.21, 126.07, 125.82,

125.67, 51.03, 29.27.



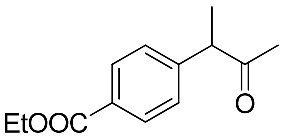
3n

Ethyl 4-(2-oxobutyl)benzoate. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02-7.99 (d, *J* = 8.4 Hz, 2H), 7.29-7.26 (d, *J* = 8.1 Hz, 2H), 4.41-4.34 (q, *J* = 7.0 Hz, 2H), 3.76 (s, 2H) 2.53-2.46 (q, *J* = 7.4 Hz, 2H), 1.41-1.37 (t, *J* = 7.1 Hz, 3H), 1.06-1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.25, 166.63, 139.70, 130.13, 129.69, 129.44, 61.19, 49.78, 35.81, 14.55, 7.95. HRMS (APCI) calcd for $C_{13}H_{16}O_3$ $[M]^+$: 220.1099; found 220.1096.



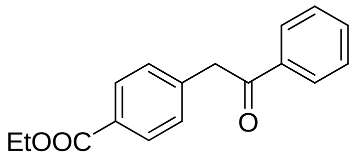
3o

Ethyl 4-(2-oxopentyl)benzoate. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02-8.00 (d, *J* = 7.8 Hz, 2H), 7.29-7.26 (d, *J* = 7.5 Hz, 2H), 4.41-4.34 (q, *J* = 6.9 Hz, 2H), 3.75 (s, 2H), 2.47-2.42 (t, *J* = 7.1 Hz, 2H), 1.65-1.53 (m, 2H), 1.41-1.37 (t, *J* = 6.9 Hz, 3H), 0.90-0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.69, 163.59, 136.59, 127.08, 126.67, 126.40, 58.16, 47.11, 41.42, 14.33, 11.54, 1 0.82. HRMS (APCI) calcd for $C_{14}H_{18}O_3$ $[M]^+$: 234.1256; found 234.1260.



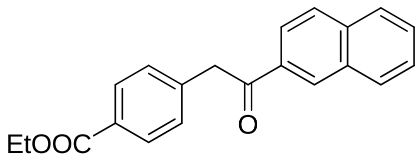
3p

Ethyl 4-(3-oxobutan-2-yl)benzoate. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04-8.01 (d, *J* = 8.1 Hz, 2H), 7.31-7.28 (d, *J* = 8.1 Hz, 2H), 4.41-4.34 (q, *J* = 7.2 Hz, 2H), 3.85-3.78 (q, *J* = 7.0 Hz, 1H), 2.06 (s, 3H), 1.42-1.37 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.20, 166.52, 145.77, 130.44, 128.08, 117.26, 61.25, 53.93, 28.78, 17.40, 14.58. HRMS (APCI) calcd for $C_{13}H_{16}O_3$ $[M]^+$: 220.1099; found 220.1102.



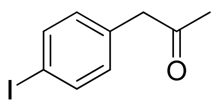
3q

Ethyl 4-(2-oxo-2-phenylethyl)benzoate. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03-7.99 (dd, J = 8.1 Hz, J = 2.1 Hz, 3H), 7.60-7.55 (t, J = 7.4 Hz, 1H), 7.49-7.44 (t, J = 7.5 Hz, 2H), 7.35-7.32 (d, J = 8.4 Hz, 2H), 7.23-7.15 (m, 1H), 4.40-4.33 (m, 4H), 1.40-1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.78, 166.34, 139.58, 136.21, 133.35, 131.83, 130.49, 129.79, 129.50, 129.06, 128.90, 128.78, 128.66, 128.46, 127.73, 60.86, 45.32, 14.26. HRMS (APCI) calcd for $C_{17}H_{16}O_3$ $[M]^+$: 268.1099; found 268.1098.



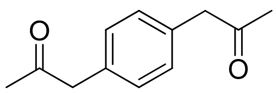
3r

Ethyl 4-(2-(naphthalen-2-yl)-2-oxoethyl)benzoate. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.05-7.85 (m, 6H), 7.63-7.53 (m, 2H), 7.39-7.37 (d, J = 8.1 Hz, 2H), 4.47 (s, 2H), 4.39-4.32 (q, J = 7.1 Hz, 2H), 1.39-1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.03, 166.64, 140.03, 135.88, 133.94, 132.67, 130.62, 130.14, 129.83, 129.42, 128.94, 128.88, 128.03, 127.14, 124.30, 61.15, 45.68, 14.57. HRMS (APCI) calcd for $C_{21}H_{18}O_3$ $[M]^+$: 268.1099; found 318.1256.



3t

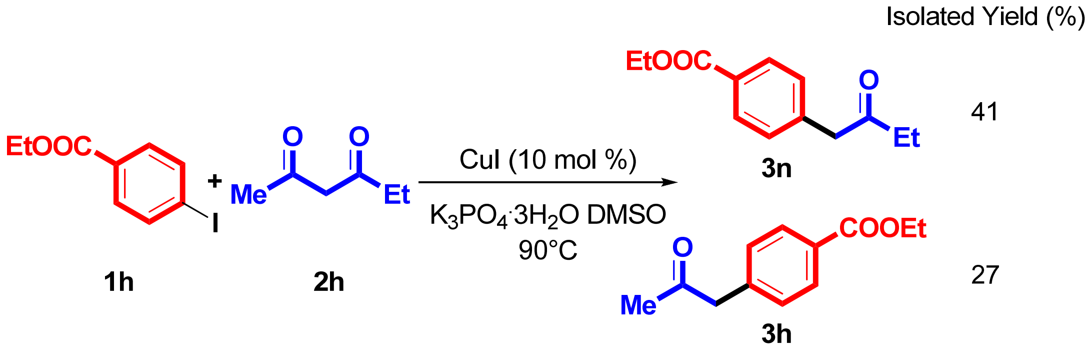
1-(4-Iodophenyl)propan-2-one. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67-7.65 (d, J = 7.8 Hz, 2H), 6.95-6.94 (d, J = 7.8 Hz, 2H), 3.65 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 205.49, 137.79, 137.69, 133.68, 131.45, 131.31, 92.56, 50.23, 29.43. HRMS (APCI) calcd for C_9H_9OI $[M]^+$: 259.9698; found 259.9696.



3u

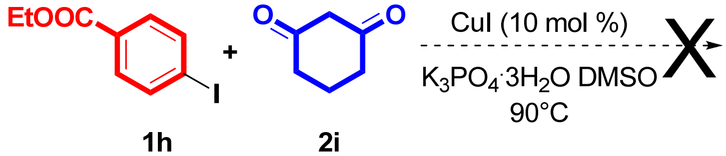
1,1'-(1,4-Phenylene)dipropan-2-one.[9] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (s, 4H), 3.68 (s, 4H), 2.16 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.19, 132.92, 129.78, 129.69, 129.60, 129.45, 50.43, 29.30.

α-Arylation of Unsymmetric β-Diketone:



When unsymmetric β-diketone hexane-2, 4-dione **2h** was employed as the nucleophile to react with **1h**, the C-C activation were also observed, which produced the two desired α-aryl ketones **3n** and **3h** in 41% and 27% yield.

α-Arylation Cyclic β-Diketone:



When cyclic β-diketone cyclohexane-1, 3-dione **2i** was employed as the nucleophile to react with **1h**, no reaction occurred under the standard reaction conditions.

General ReactIR Experimental Details

For the ReactIR kinetic experiments, the reaction spectra were recorded using a IC 10 from Mettler-Toledo AutoChem fitted with a diamond-tipped probe. Data manipulation was carried out using the iC IR software, version 1. 05.

The Experimental Details:

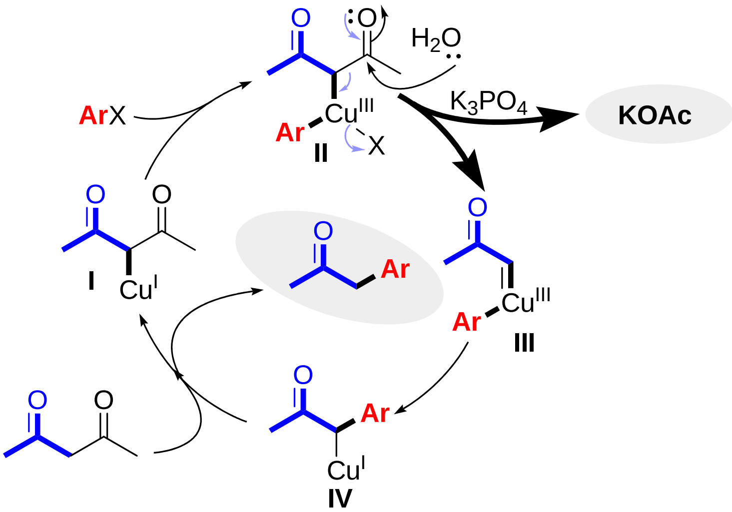
The reaction was carried out as follows: a three necked reaction vessel was fitted with a magnetic stirring bar. The IR probe was inserted through an adapter into the middle neck; the other two necks were capped by septa for injections and a nitrogen line. The reaction vessel was kept 90 ^{o}C. Following evacuation under vacuum and flushing with nitrogen for three times, the three necked vessel was charged with 3.0 mL DMSO solution of iodobenzene **1a** (1.0 mmol), acetylacetone **2a** (3.0 mmol), CuI (0.1 mmol) and $K_3PO_4{\cdot}3H_2O$ (3.0 mmol). Then the data collection was started and IR spectra were recorded over the course of the reaction.

Data Analysis:

Based on the IR data gained in the above reaction of **1a** and **2a**, we delighted to see that the kinetic profiles not only clearly revealed the consumption of **2a** and the formation of **1c** (afford 85% GC yield for 12 h), but also a new species increasing at peak 1583 cm^{-1} which was unambiguously assigned as KOAc based upon comparison of its ConcIRT spectrum to the authentic sample of KOAc.

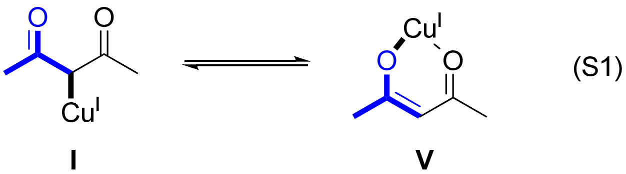
Putative Mechanism Discussion

The putative catalytic cycle **A** has been listed in the paper (Scheme 2). Cu(I)-complex **I** could be oxidatively added to the ArX to form a Cu(III)-intermediate **II**. In the presence of H_2O, the C-C bond activation/cleavage occurred, which led to the formation of intermediate **III**, and the release of KOAc. Reductive elimination of intermediate **III** could produce the other Cu(I)-intermediate **IV**, which would finally produce the desired α-aryl ketones by reacting with the diketone, and regenerate the Cu(I)-intermediate **I** species for the next catalytic cycle.



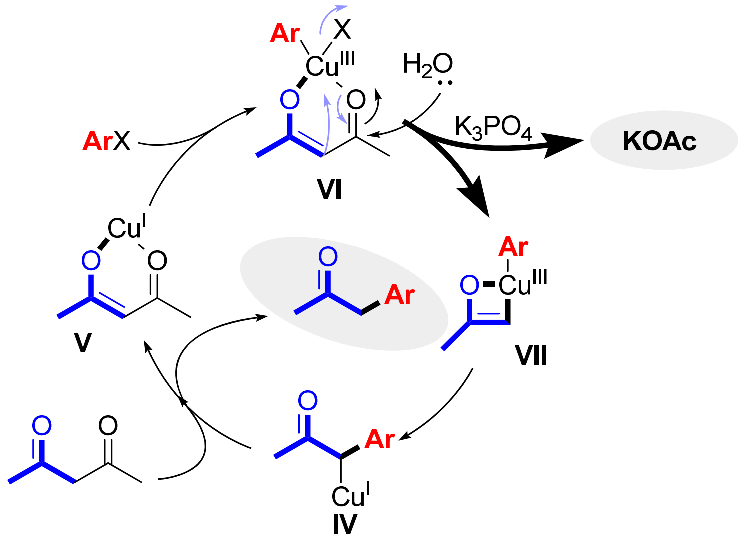
A

It is known that there is a equilibrium between Cu(I)-complex **I** and copper(I) enolate **V** (eq. S1).



Consequently, catalytic cycle **B** is also another possible pathway to achieve this arylation/C-C activation. Copper(I) enolate **V** could be oxidatively added to the ArX to form a Cu(III)-intermediate **VI**. In the presence of H_2O, the C-C bond activation/cleavage occurred, which led to the formation of a 4-membered copper(III) ring complex **VII** and the release of KOAc. Reductive elimination of intermediate

VII could produce the other Cu(I)-intermediate **IV**, which would finally produce the desired α-aryl ketones by reacting with diketone, and regenerated the Cu(I)-intermediate **V** species for the next catalytic cycle.



B

Reference

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(5) Min, R. S.; Aksenov, V. S.; Vinogradov, M. G.; Nikishin, G. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2292-2295.

(6) Inaba, S.; Rieke, R. D. *J. Org. Chem.* **1985**, *50*, 1373-1381.

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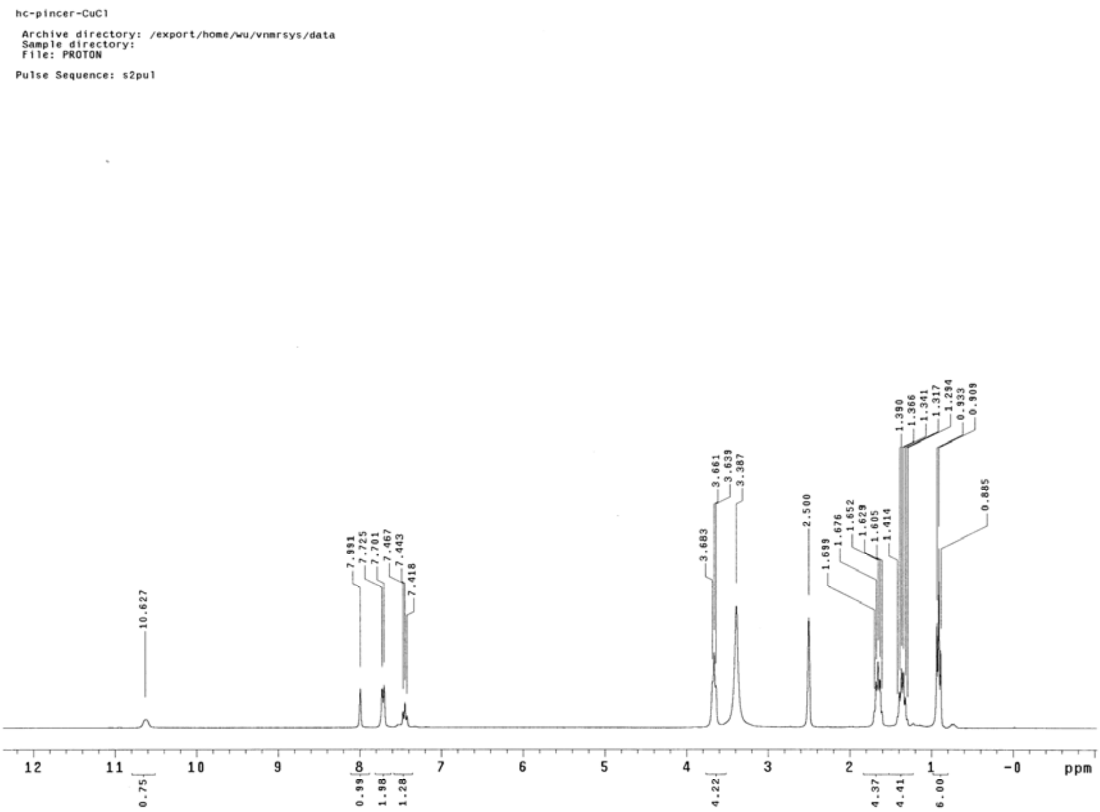
(8) Wright, S. W.; Hageman, D. L.; McClure, L. D. *J. Org. Chem.* **1994**, *59*, 6095-6097.

(9) Bartoli, S.; De Nicola, G.; Roelens, S. *J. Org. Chem.* **2003**, *68*, 8149-8156.

Spectrum

(pincer thioamide)-CuCl



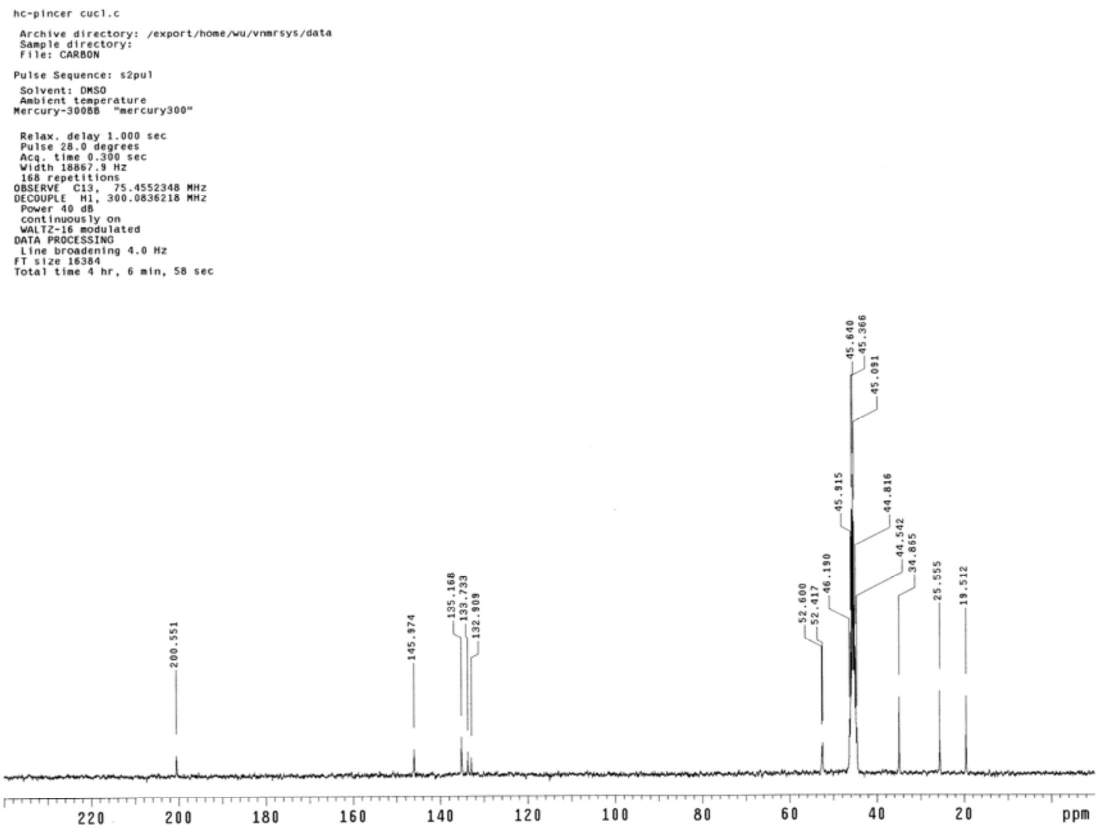


Table 2

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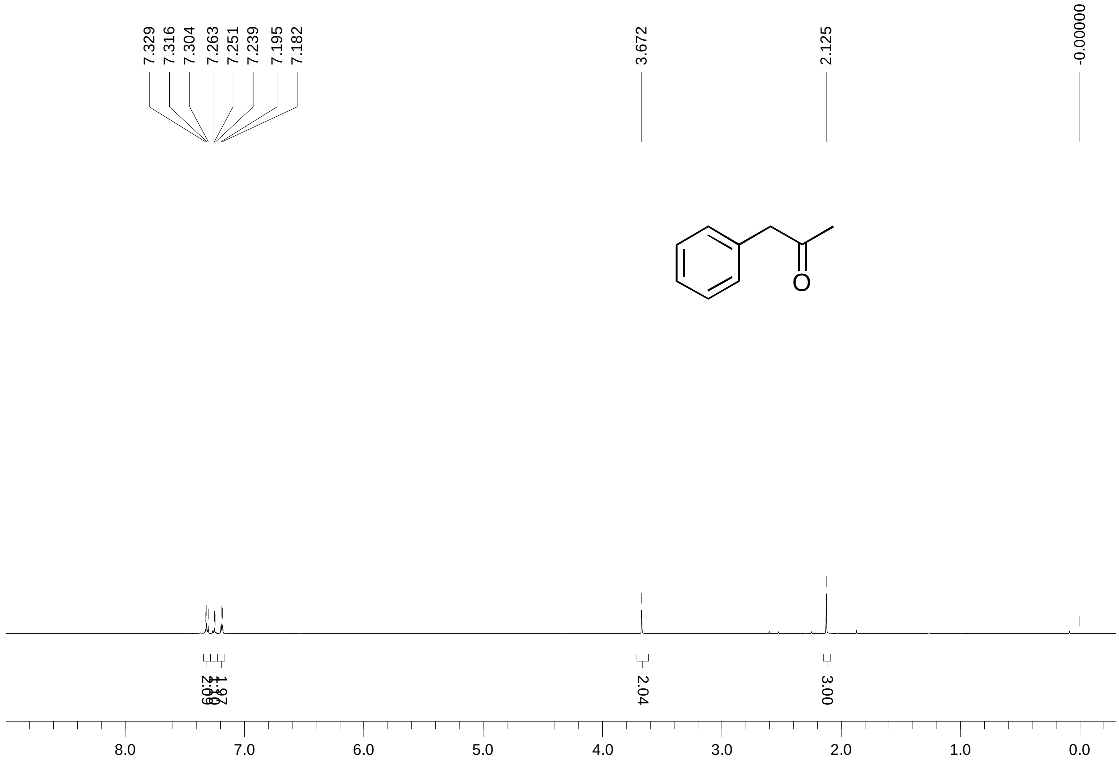
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7.263
7.251
7.239
7.195
7.182
3.672
2.125
-0.00000
O
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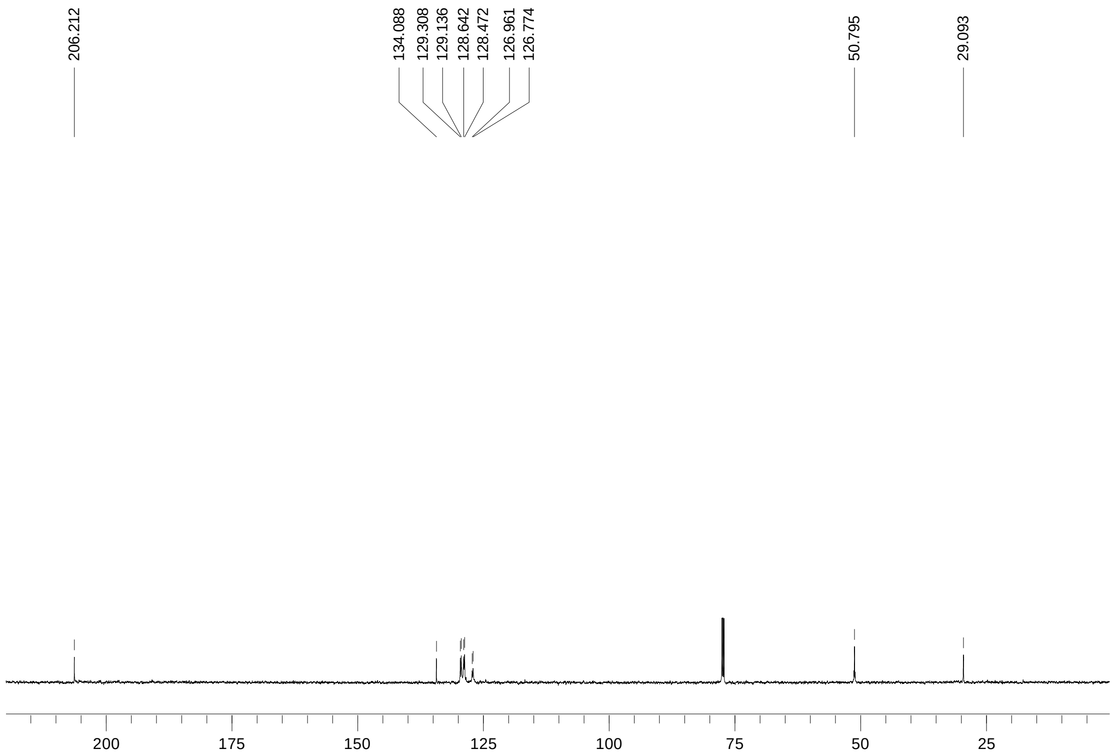
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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134.088
129.308
129.136
128.642
128.472
126.961
126.774
50.795
29.093
200
175
150
125
100
75
50
25

3b


7.138
7.125
7.086
7.072
3.636
2.323
2.124
-0.000
O
2.04
3.04
3.00
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7.0
6.0
5.0
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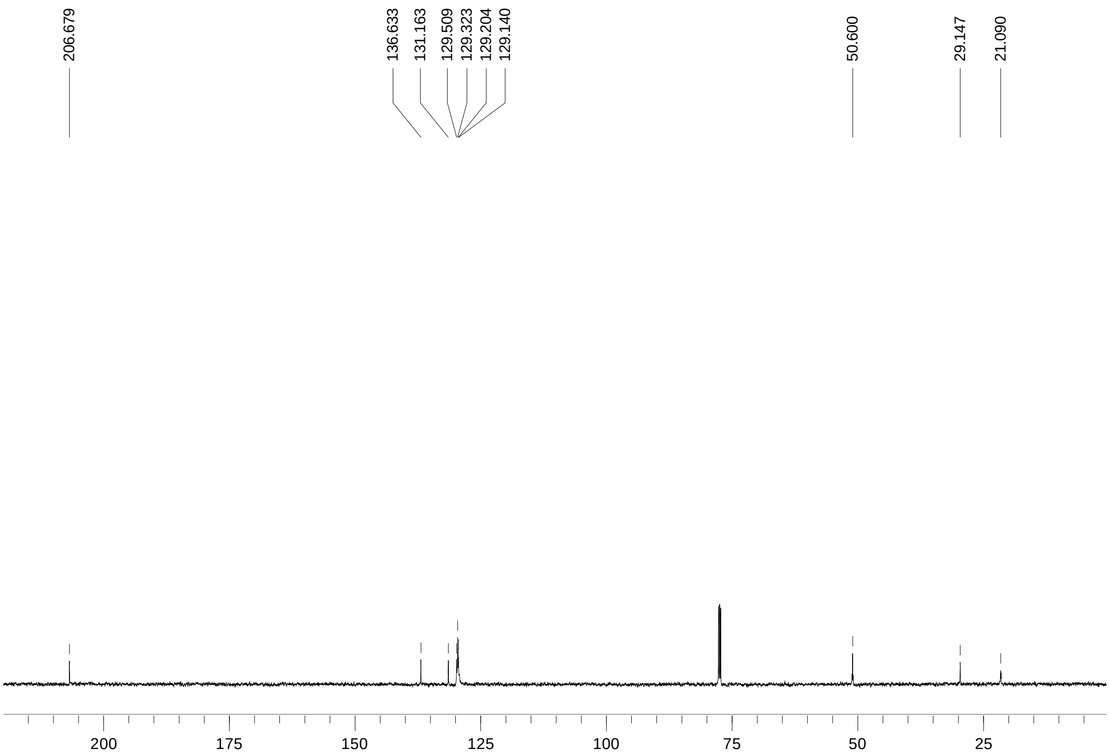
3.0
2.0
1.0
0.0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21.090
200
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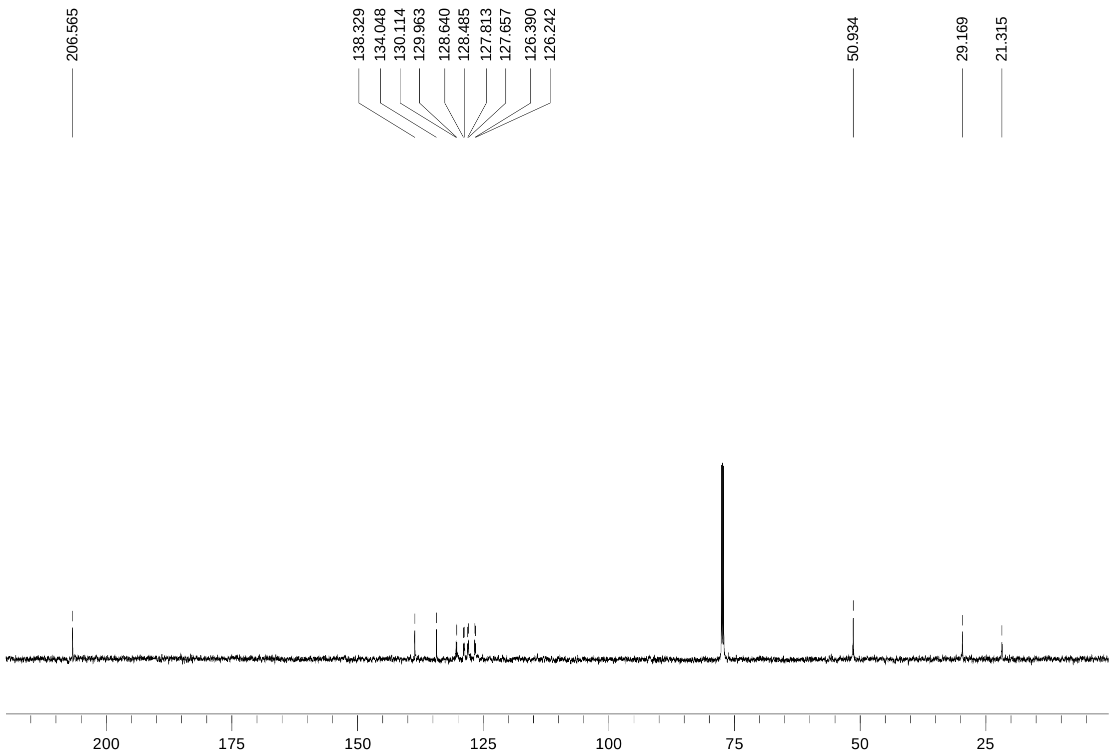
150
125
100
75
50
25

3c


7.251
7.232
7.219
7.207
7.086
7.074
7.016
7.007
6.994
3.648
2.337
2.142
0.000
O
1.02
2.04
3.03
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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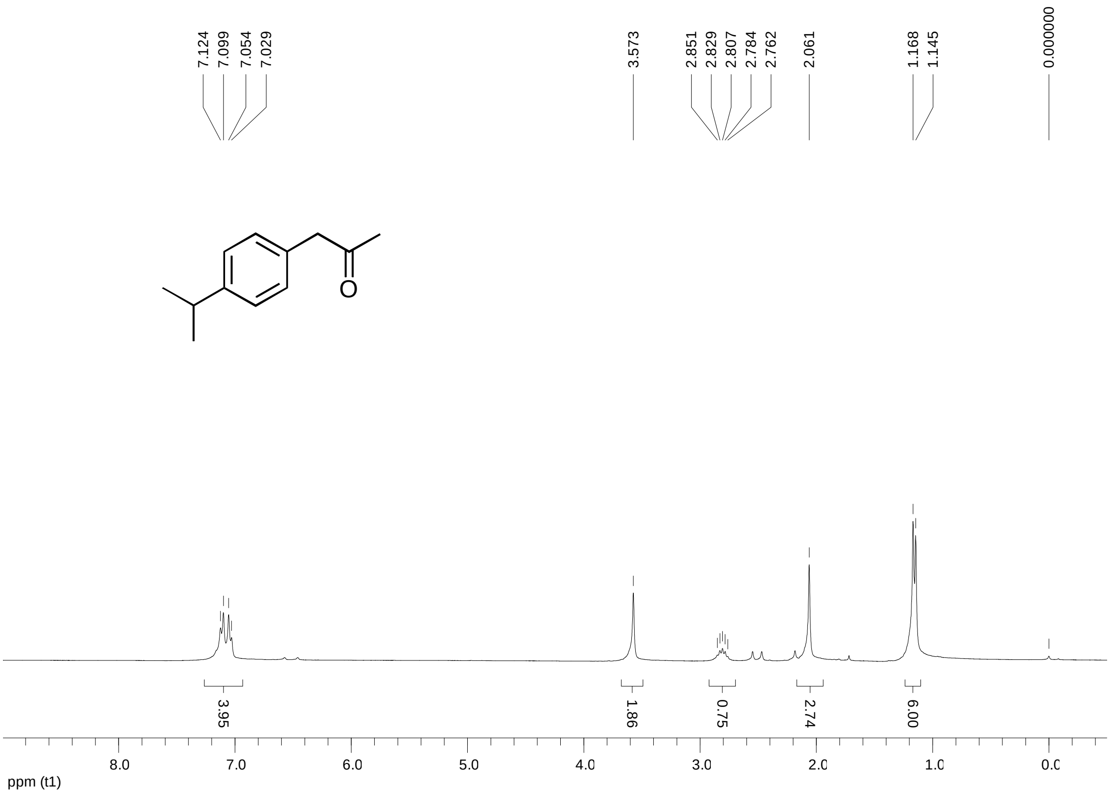
130.114
129.963
128.640
128.485
127.813
127.657
126.390
126.242
50.934
29.169
21.315
200
175
150
125
100
75
50
25

3d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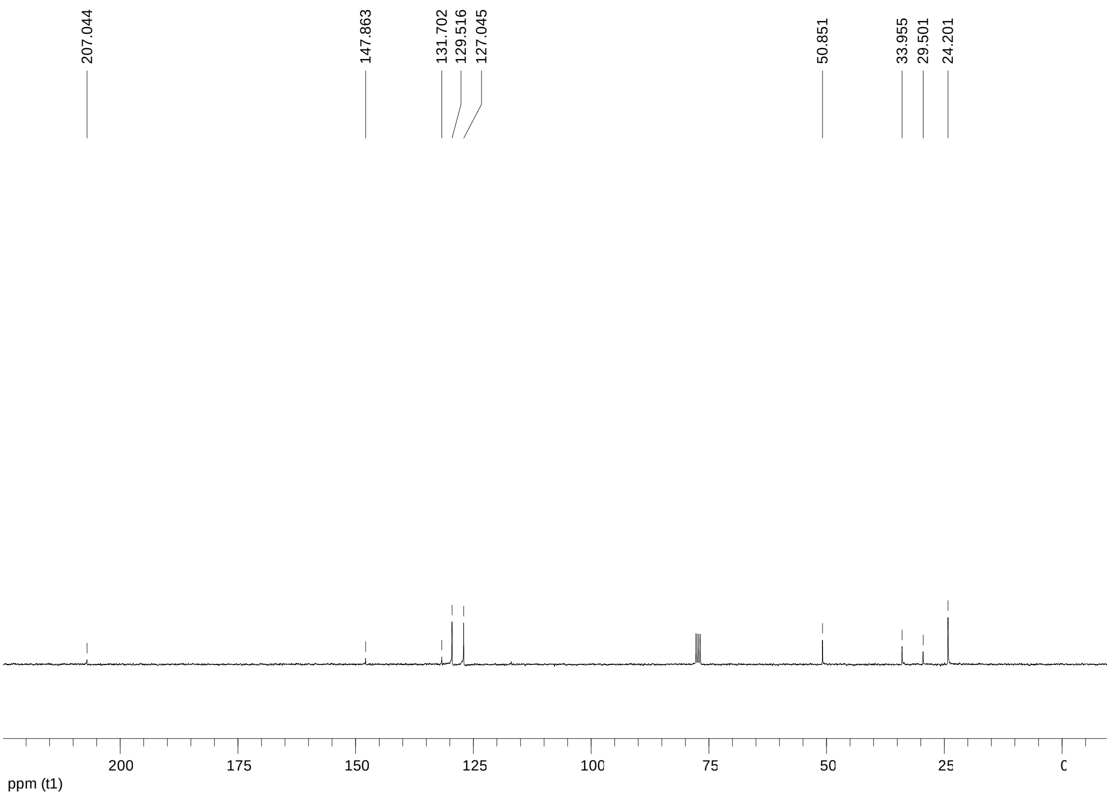
7.099
7.054
7.029
3.573
2.851
2.829
2.807
2.784
2.762
2.061
1.168
1.145
0.000000
O
3.95
1.86
0.75
2.74
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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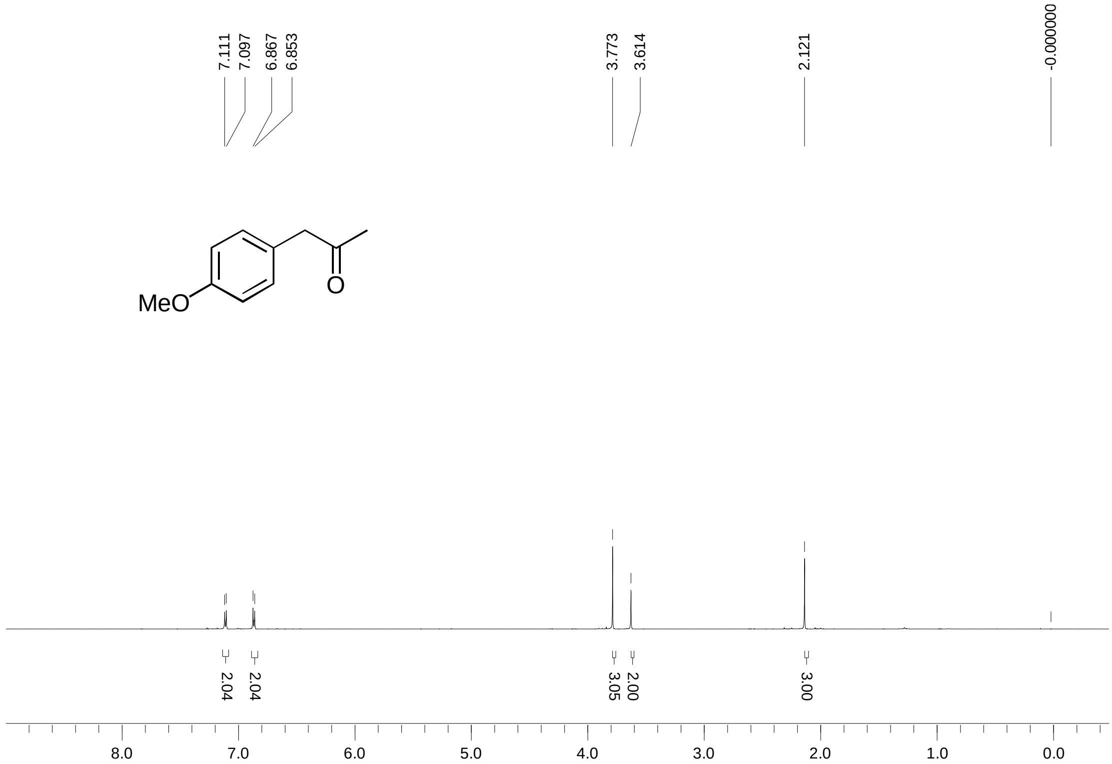
147.863
131.702
129.516
127.045
50.851
33.955
29.501
24.201
200
175
150
125
100
75
50
25
0
ppm (t1)

3e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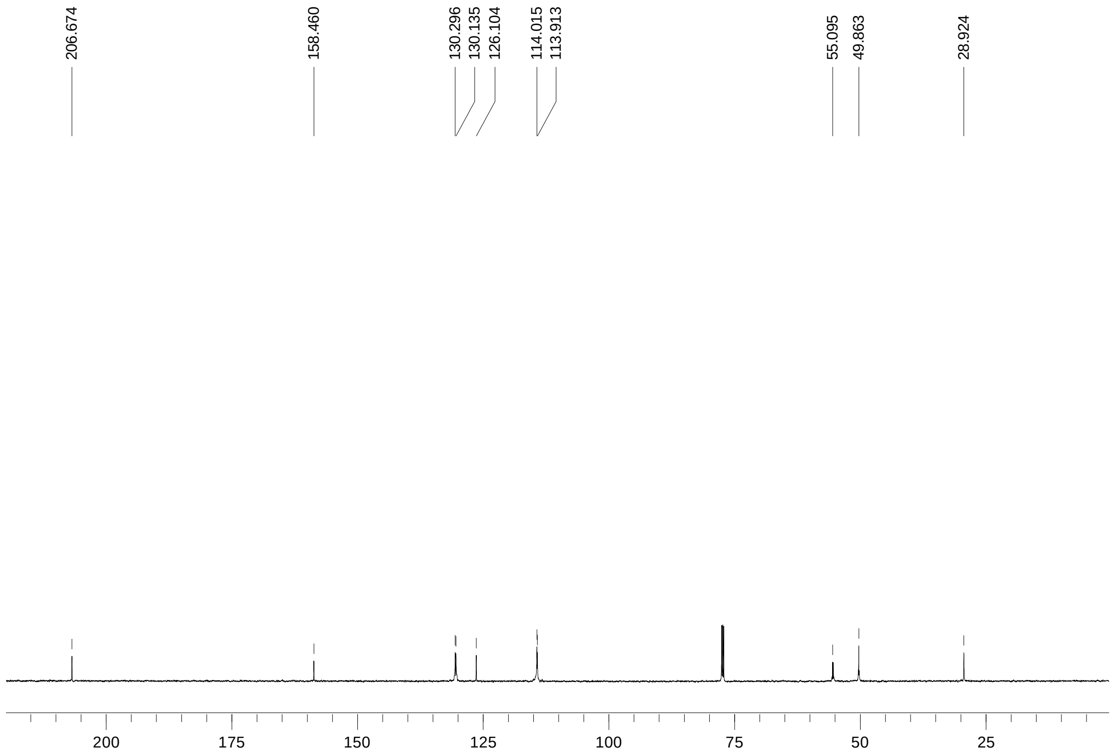
7.097
6.867
6.853
3.773
3.614
2.121
-0.000000
MeO
O
2.04
2.04
3.05
2.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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126.104
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55.095
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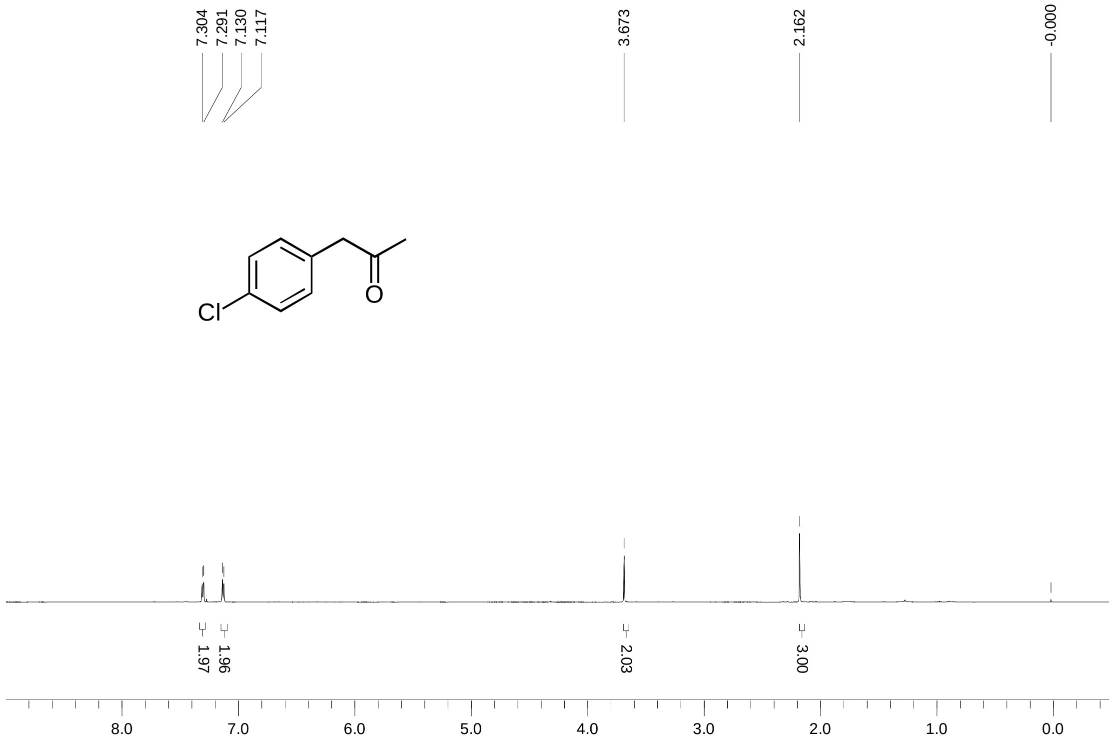
175
150
125
100
75
50
25

3f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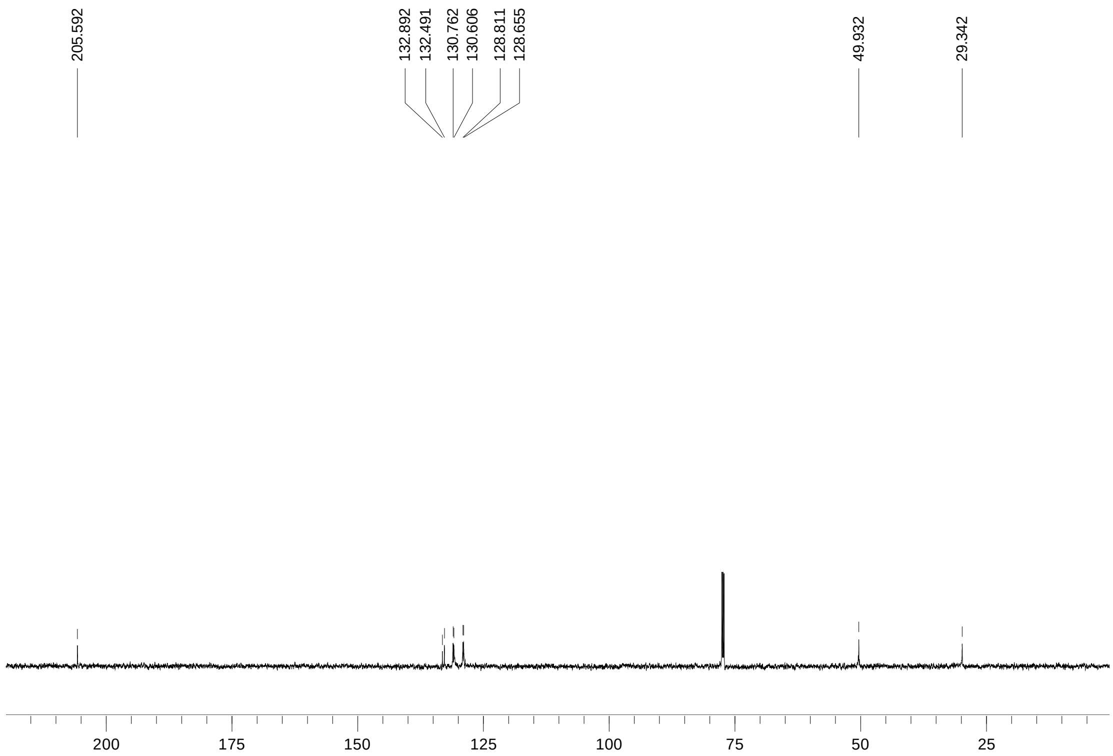
7.117
3.673
2.162
-0.000
Cl
O
1.97
1.96
2.03
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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132.892
132.491
130.762
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128.811
128.655
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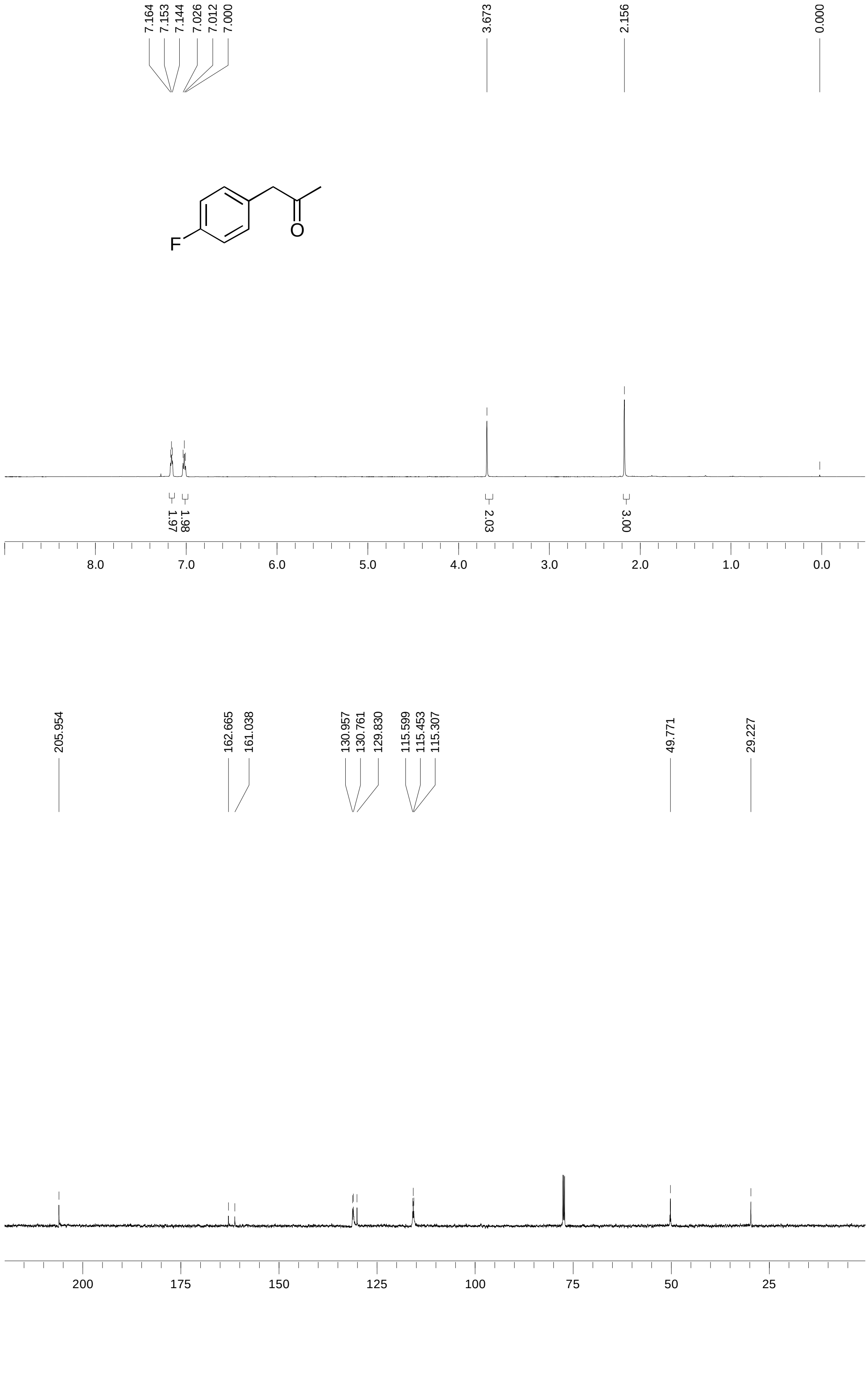
175
150
125
100
75
50
25

3g



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7.153
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7.012
7.000
3.673
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0.000
F
O
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1.98
2.03
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
205.954
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130.957
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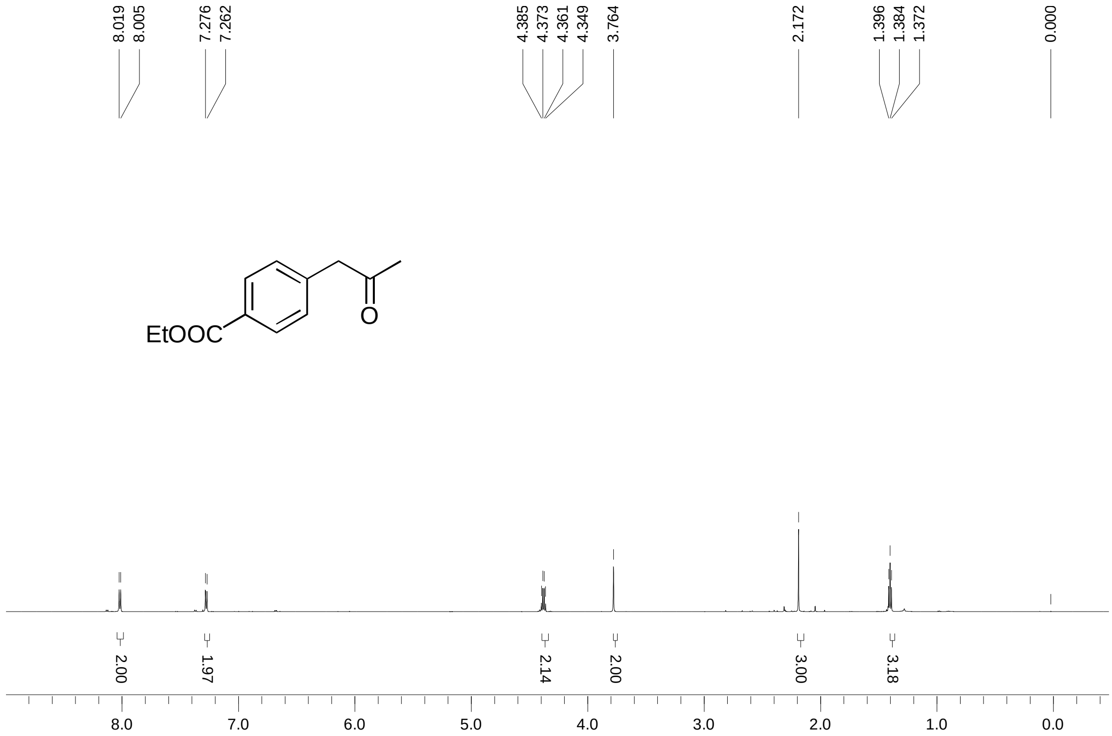
175
150
125
100
75
50
25

3h


EtOOC
O
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8.005
7.276
7.262
4.385
4.373
4.361
4.349
3.764
2.172
1.396
1.384
1.372
0.000
2.00
1.97
2.14
2.00
3.00
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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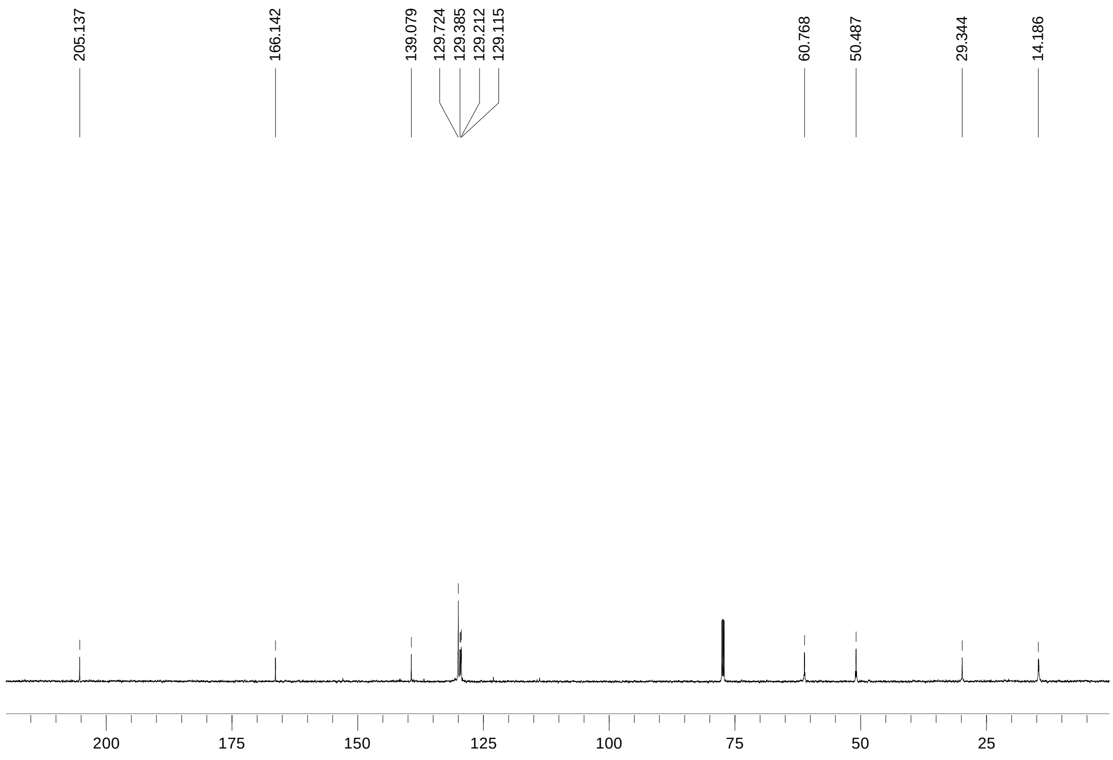
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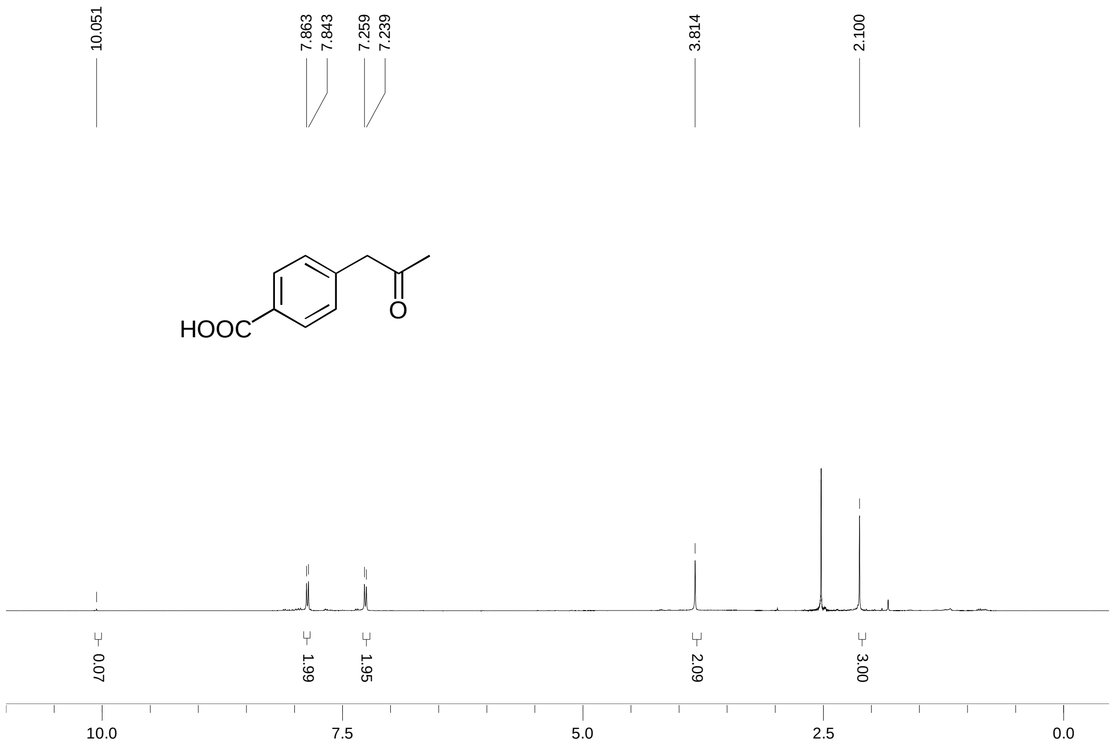
175
150
125
100
75
50
25

3i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3.814
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HOOC
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3.00
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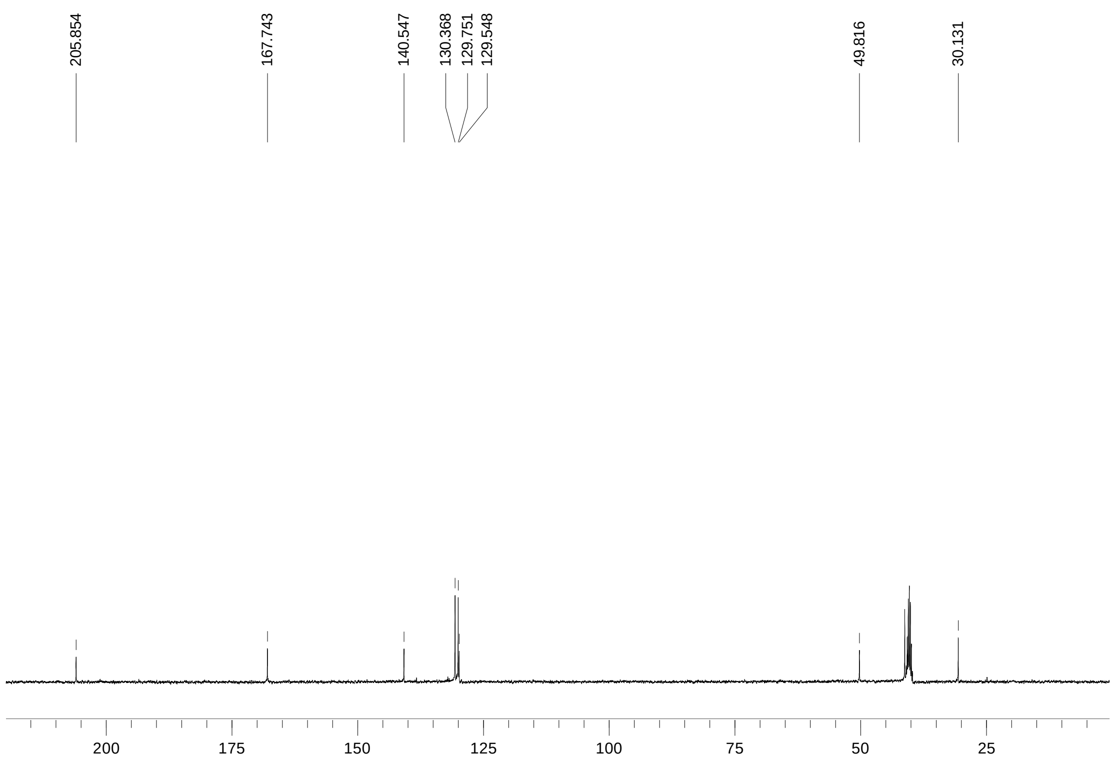
7.5
5.0
2.5
0.0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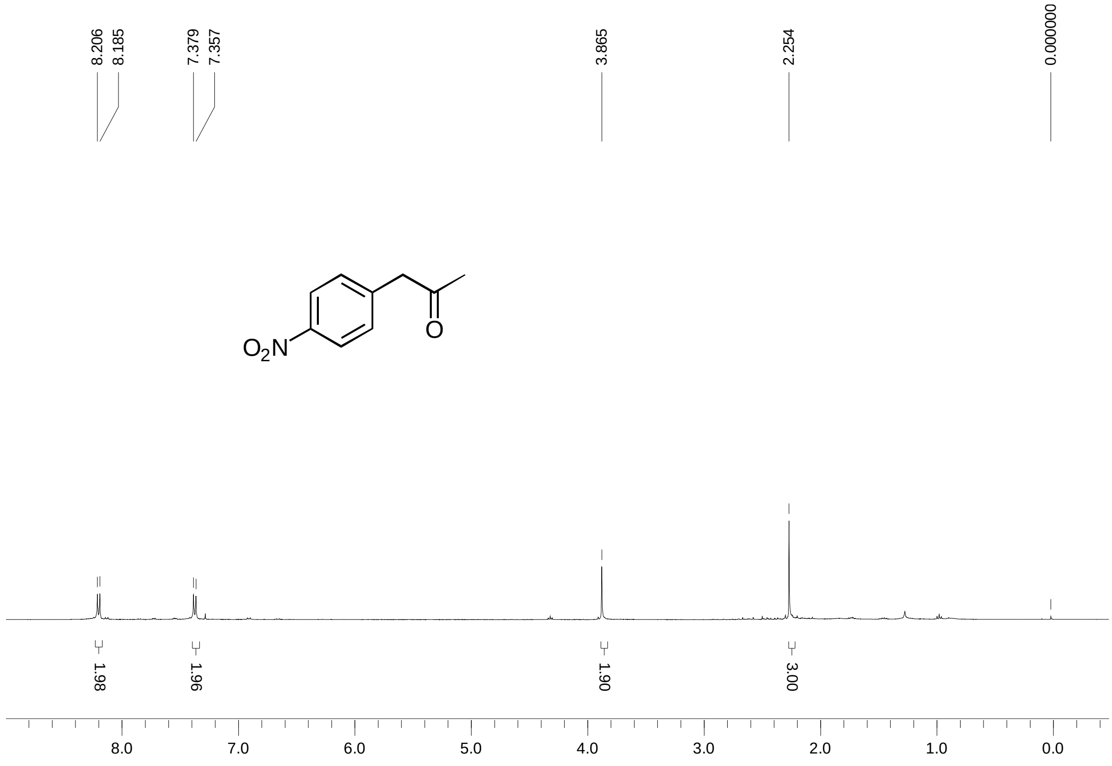
49.816
30.131
200
175
150
125
100
75
50
25

3j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1.98
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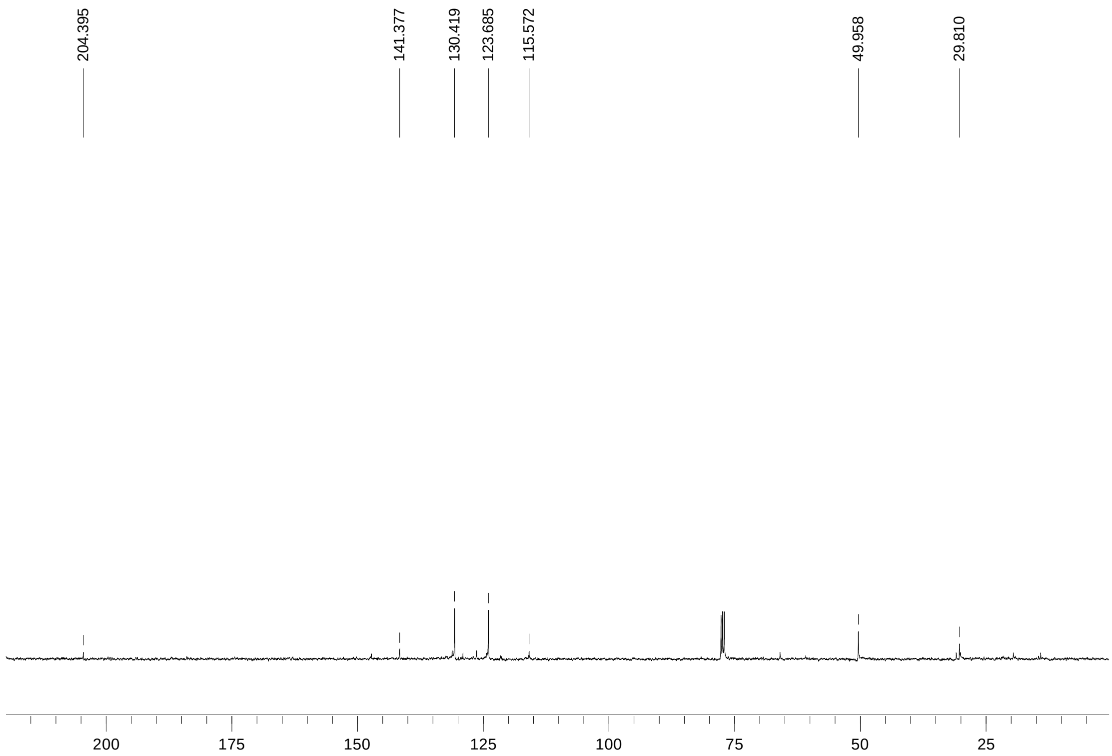
5.0
4.0
3.0
2.0
1.0
0.0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115.572
49.958
29.810
200
175
150
125
100
75
50
25

3k


7.576
7.563
7.558
7.545
7.432
7.419
7.406
7.339
7.327
7.315
7.264
7.251
3.718
2.172
0.000000
Ph
O
4.04
2.10
2.07
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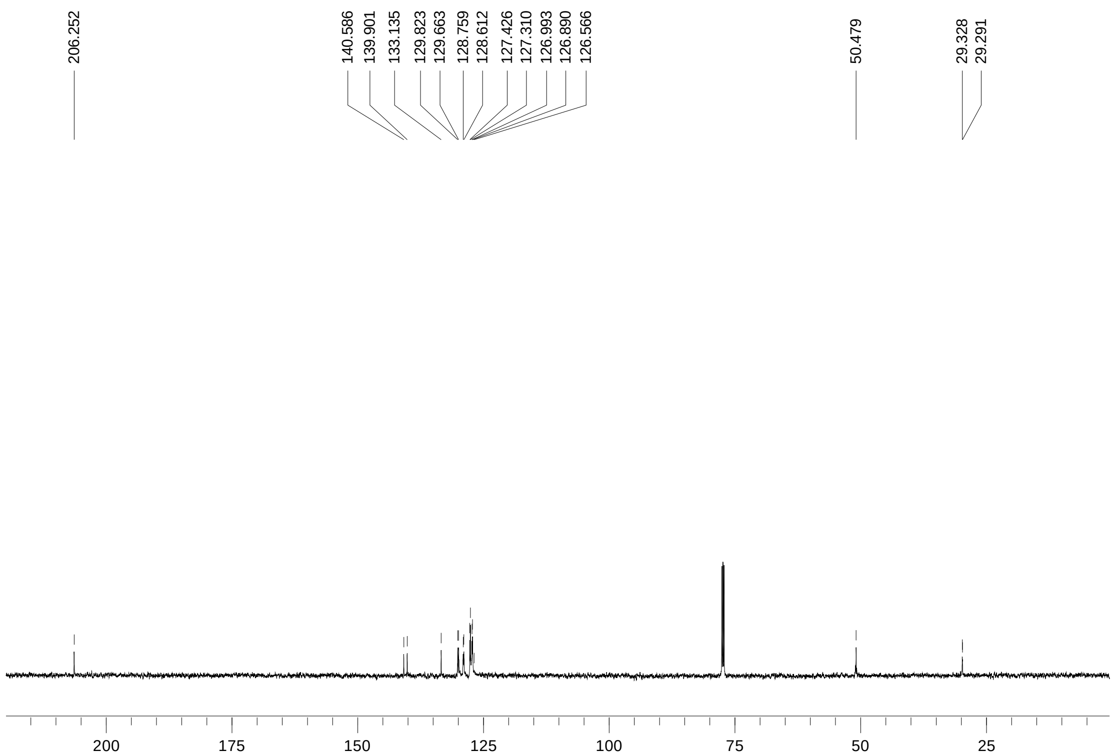
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125
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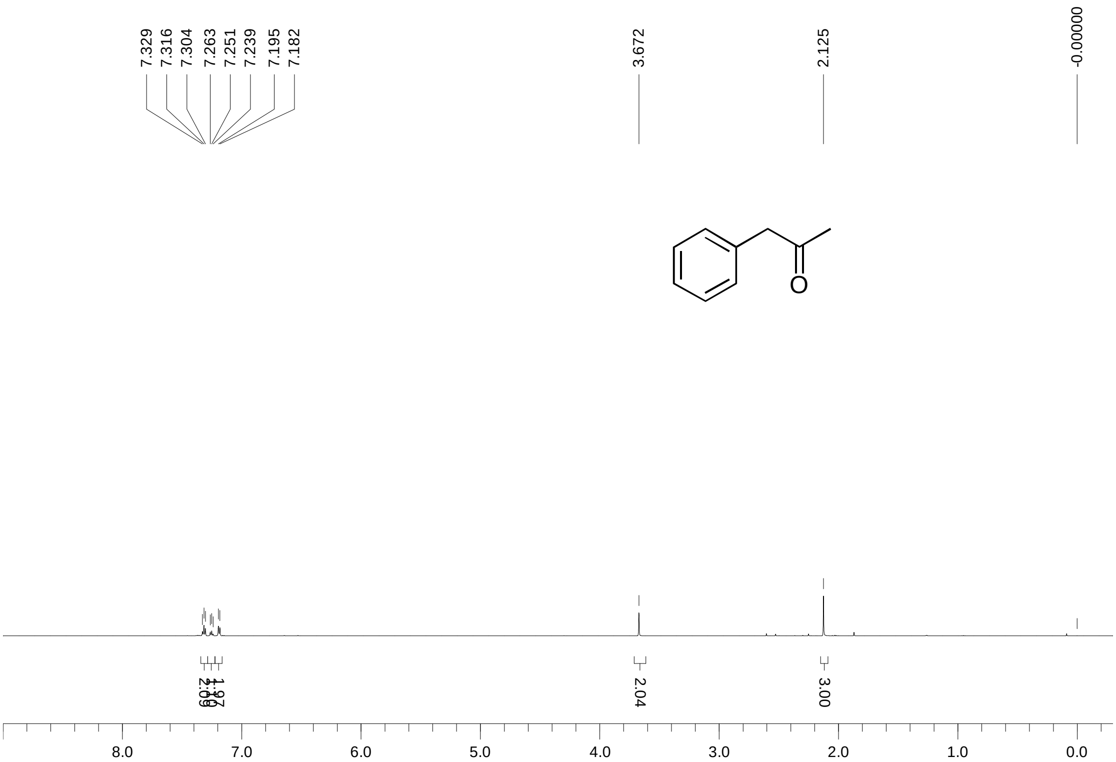
75
50
25

Table 3

3a



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7.263
7.251
7.239
7.195
7.182
3.672
2.125
-0.00000
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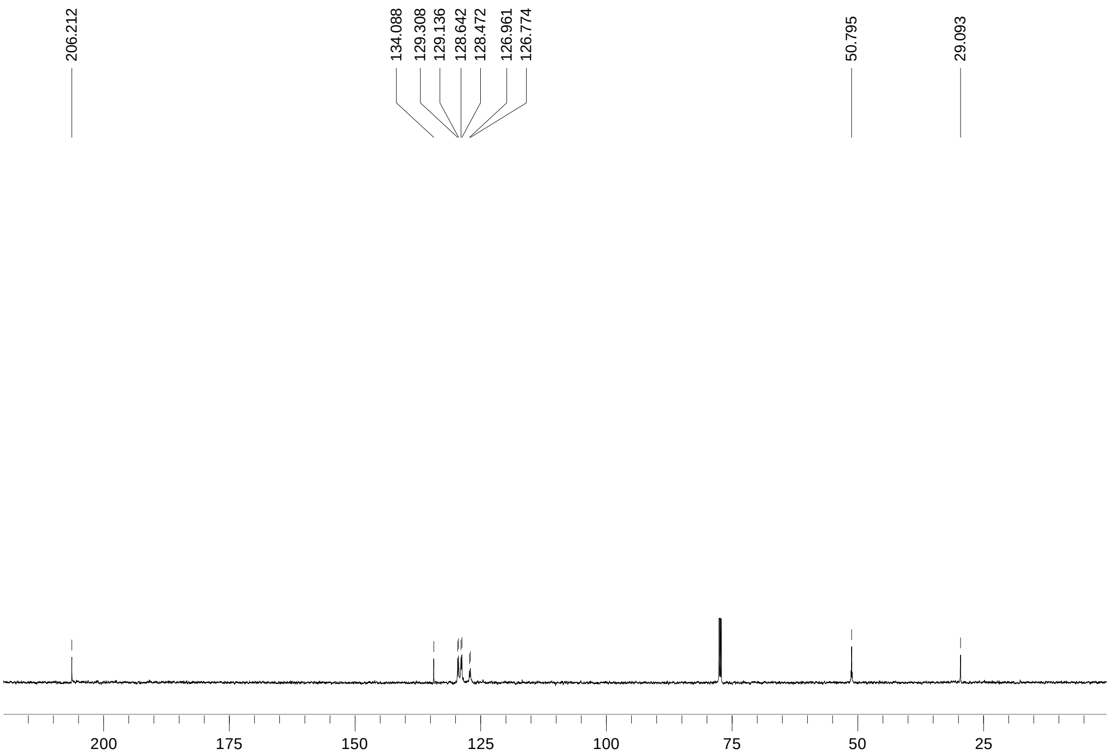
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



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129.308
129.136
128.642
128.472
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126.774
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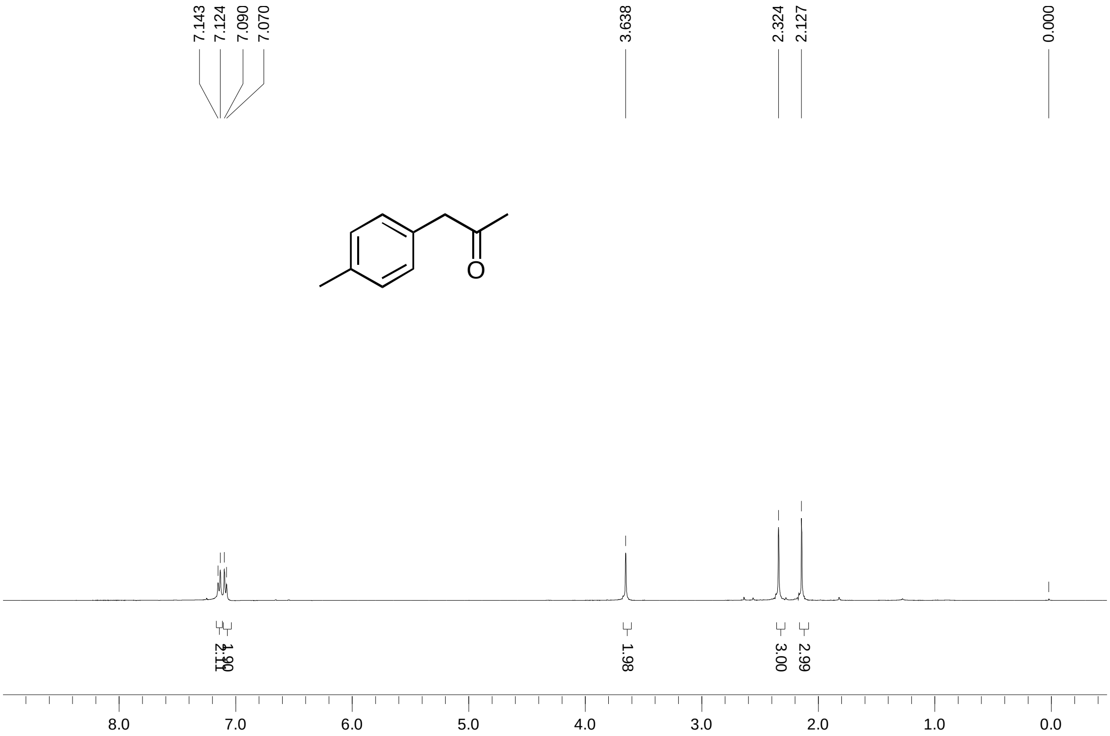
150
125
100
75
50
25

3b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1.90
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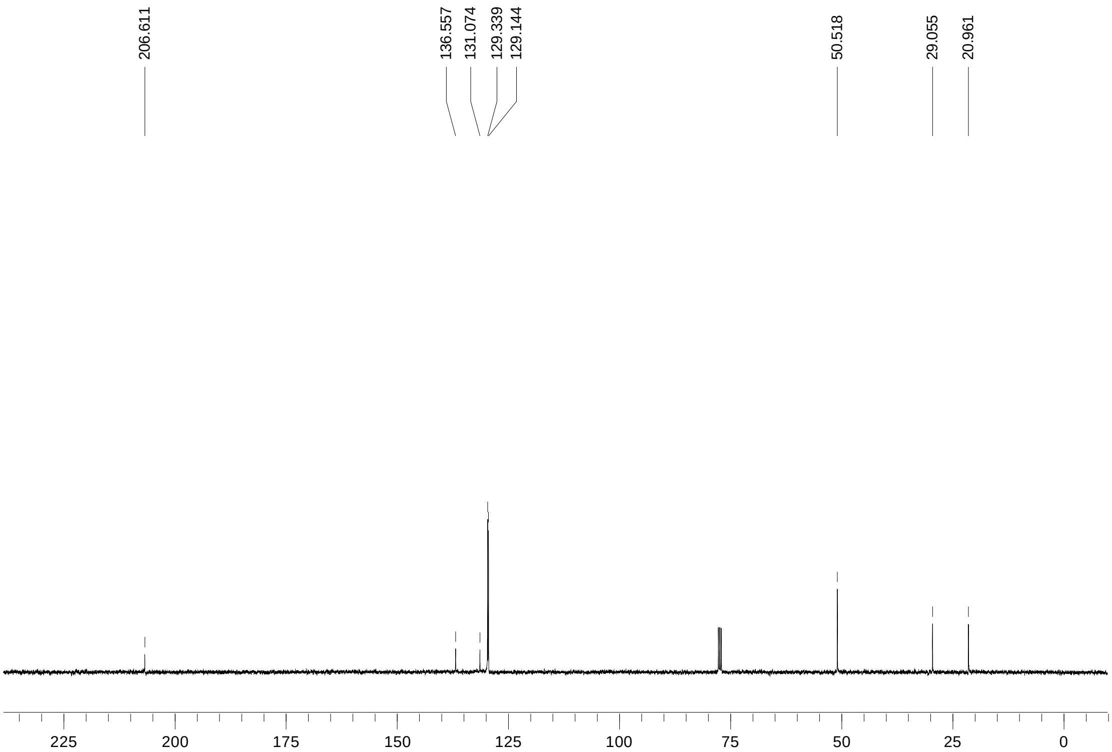
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
O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225
200
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150
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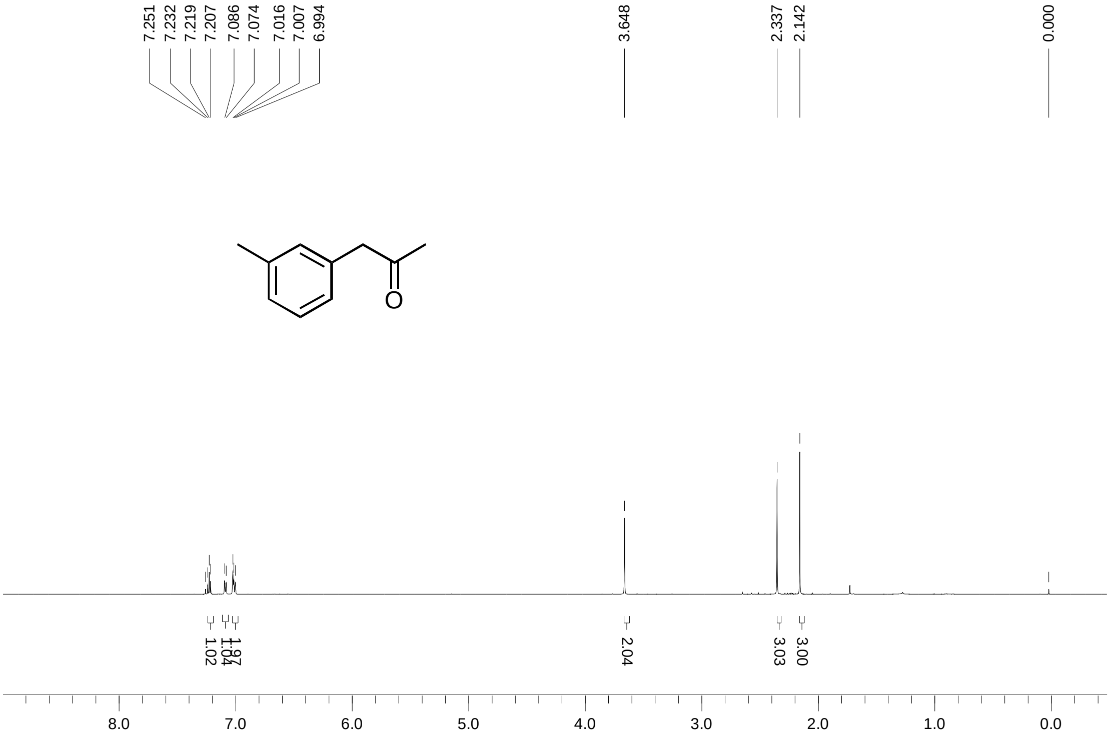
100
75
50
25
0

3c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7.232
7.219
7.207
7.086
7.074
7.016
7.007
6.994
3.648
2.337
2.142
0.000
O
1.02
1.04
1.97
2.04
3.03
3.00
8.0
7.0
6.0
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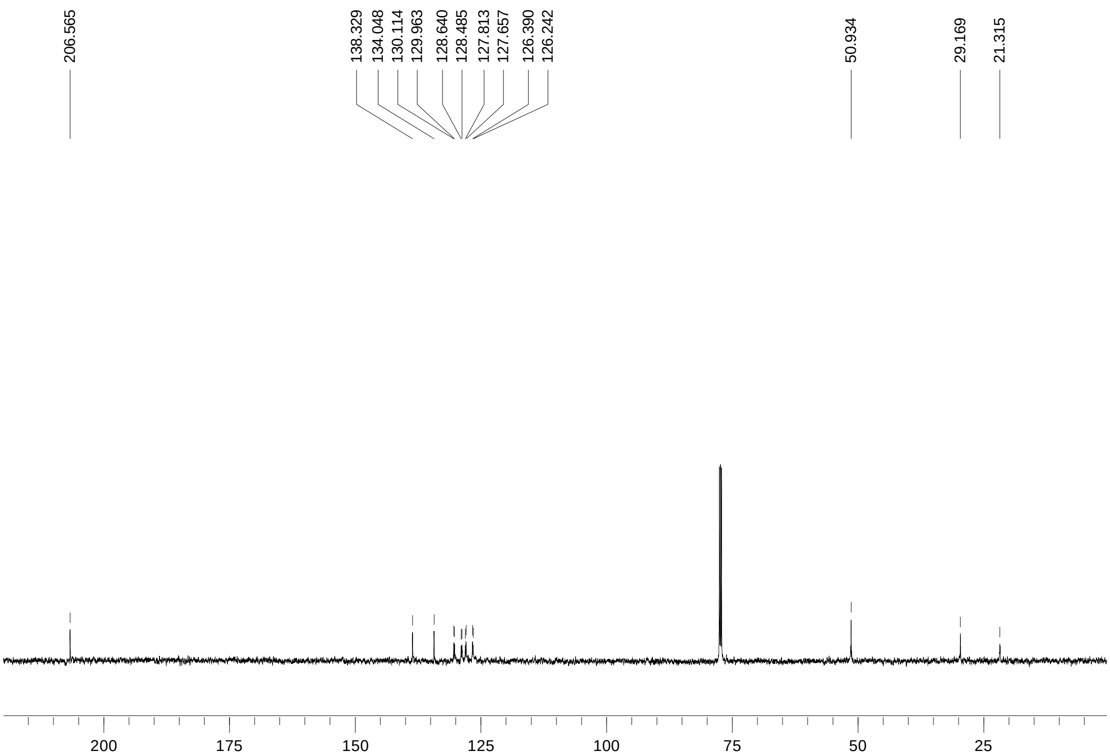
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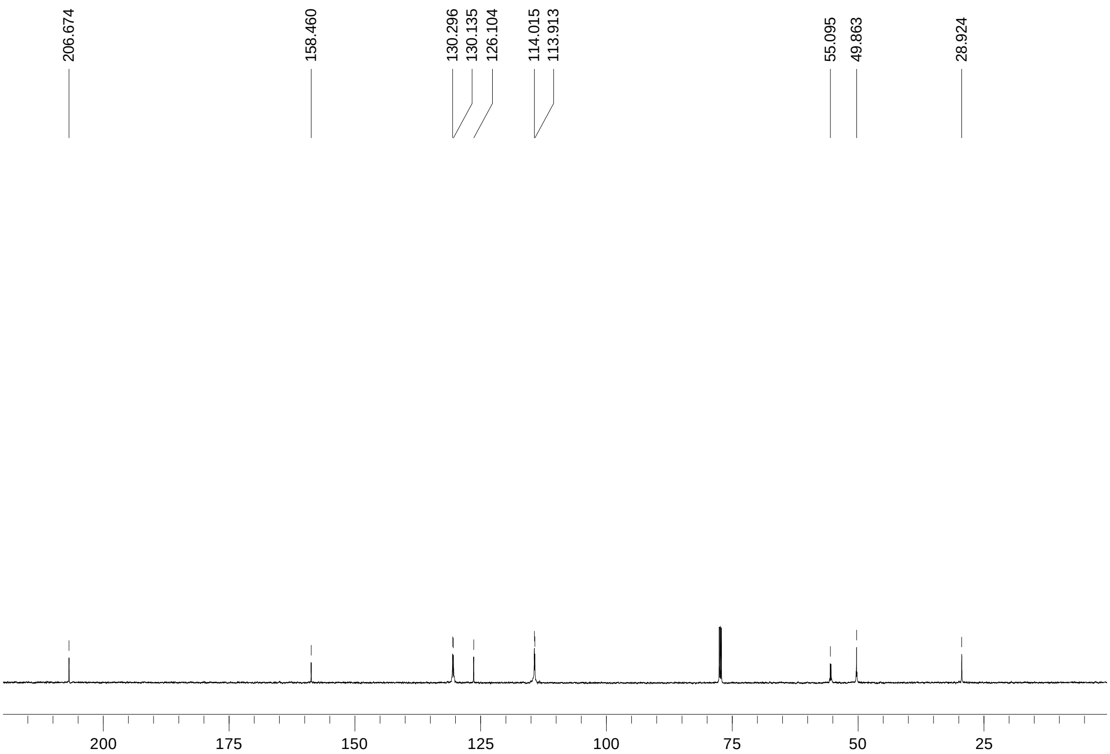
130.114
129.963
128.640
128.485
127.813
127.657
126.390
126.242
50.934
29.169
21.315
200
175
150
125
100
75
50
25

3e

7.111
7.097
6.867
6.853
3.773
3.614
2.121
-0.000000
MeO
O
2.04
2.04
3.05
2.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



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158.460
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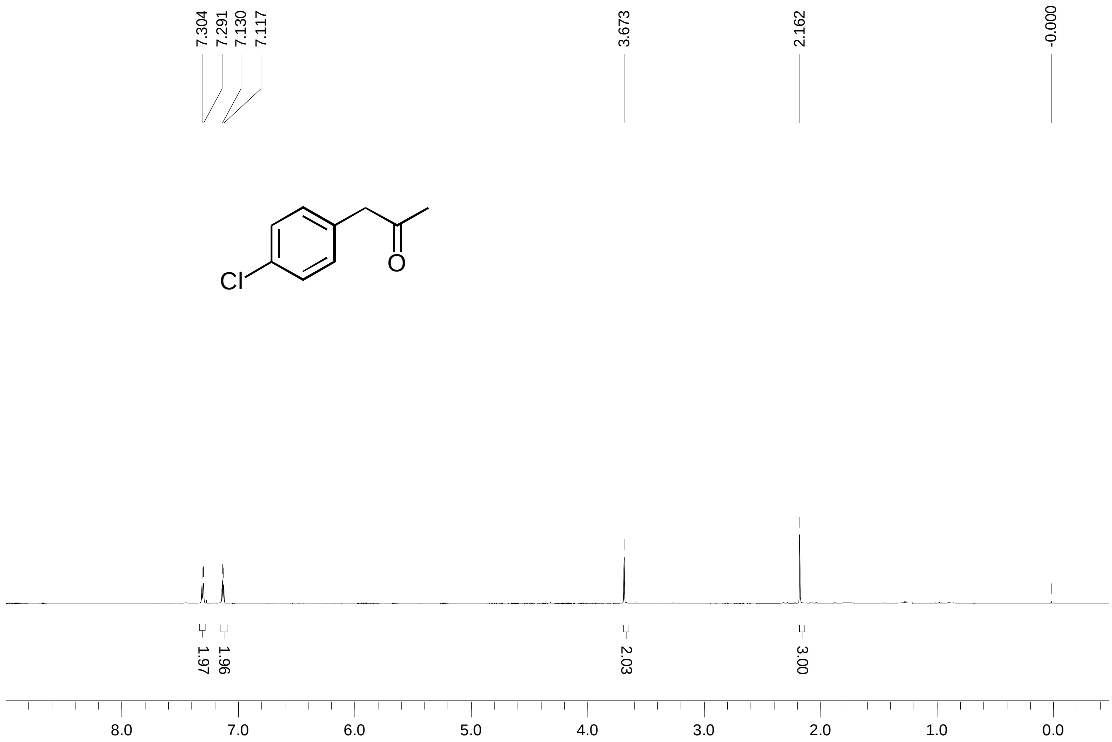
130.135
126.104
114.015
113.913
55.095
49.863
28.924
200
175
150
125
100
75
50
25

3f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7.130
7.117
3.673
2.162
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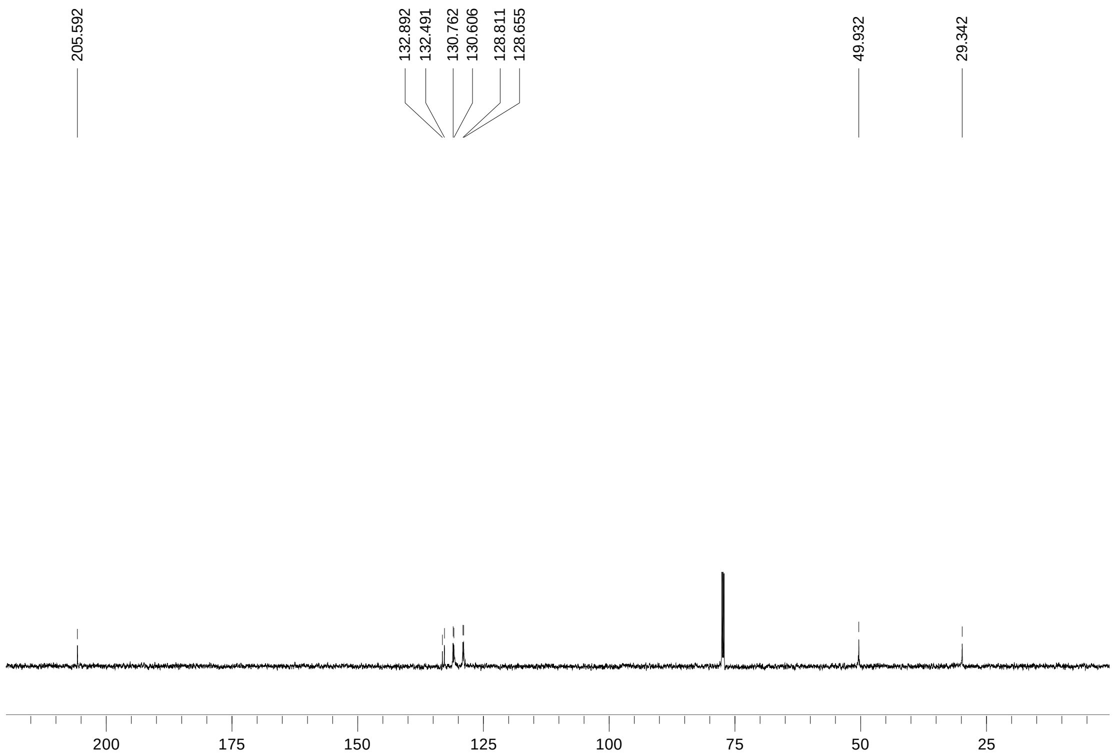
Cl
O
1.97
1.96
2.03
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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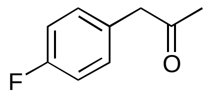
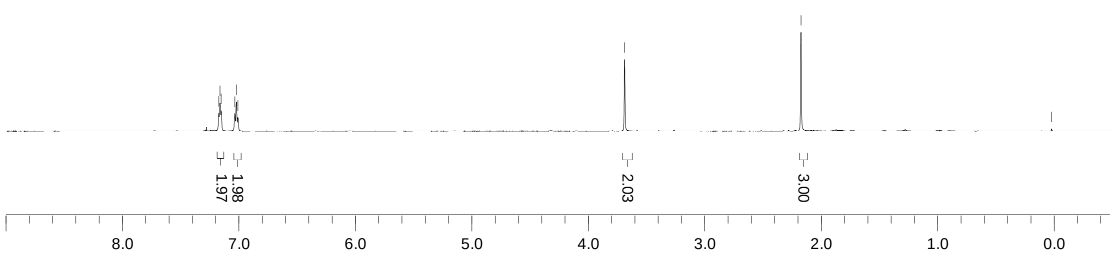
132.892
132.491
130.762
130.606
128.811
128.655
49.932
29.342
200
175
150
125
100
75
50
25

3g


F
O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8.0
7.0
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4.0
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1.0
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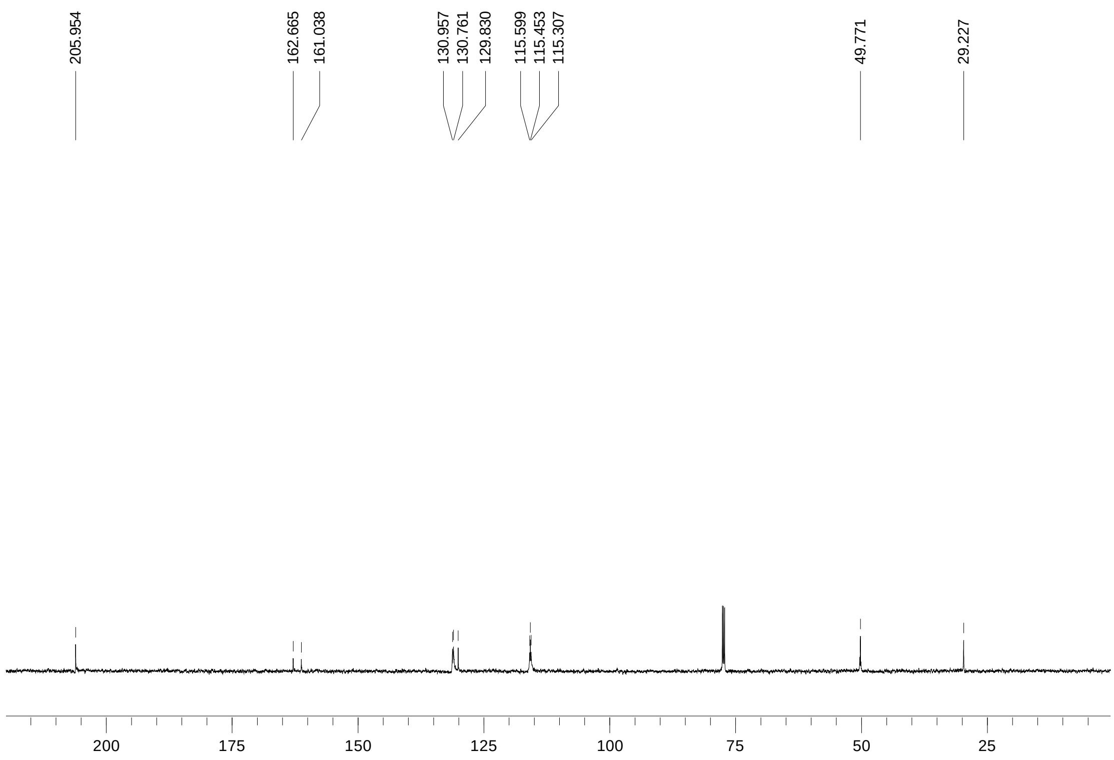
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161.038
130.957
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129.830
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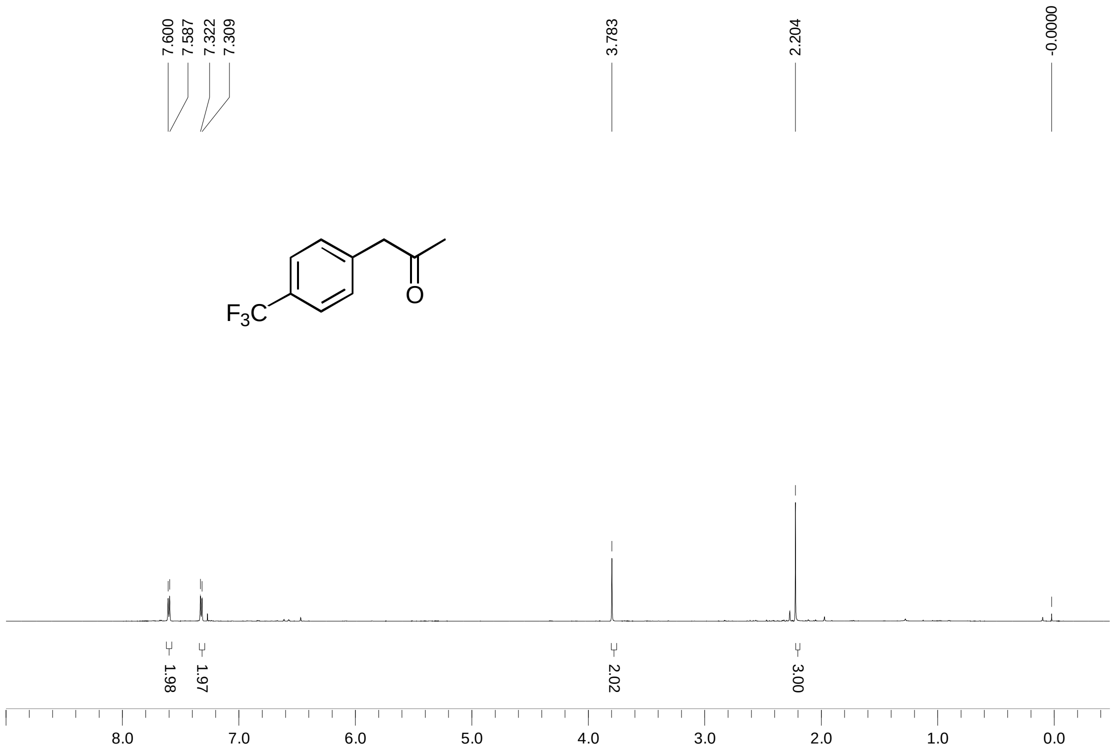
115.453
115.307
49.771
29.227
200
175
150
125
100
75
50
25

3l



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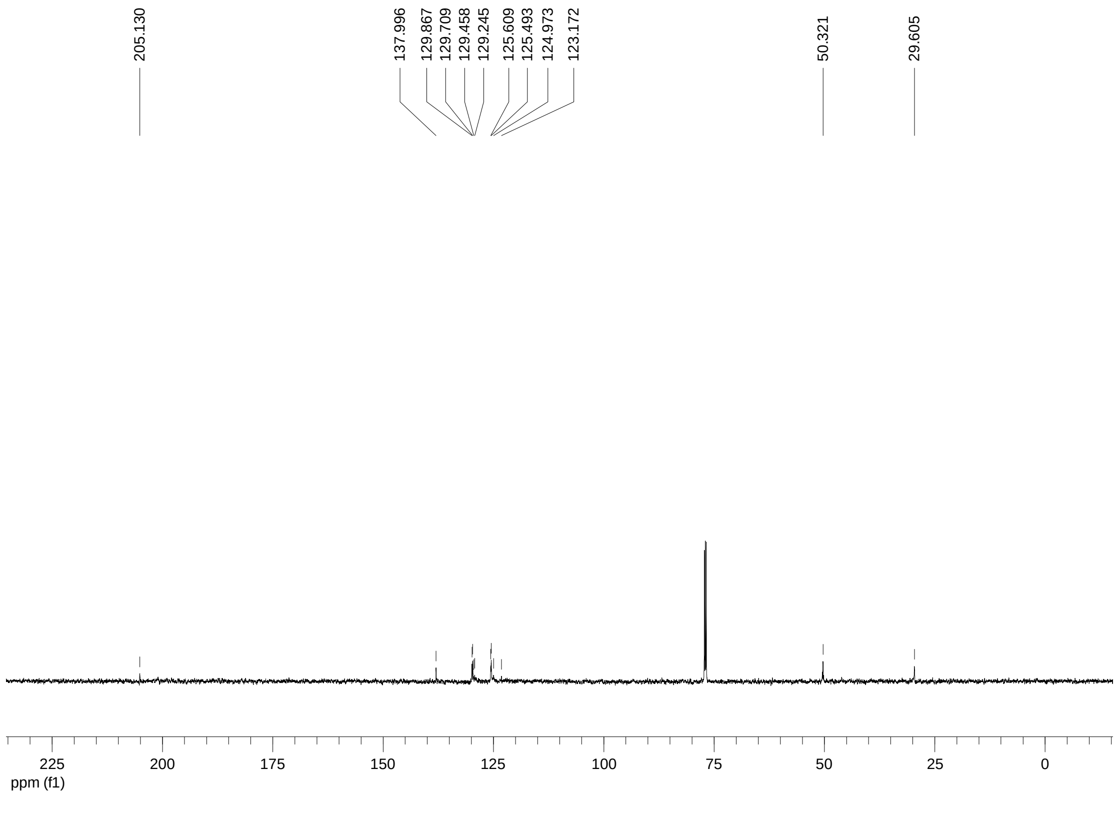
7.322
7.309
3.783
2.204
-0.0000
F3C
O
1.98
1.97
2.02
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



205.130
137.996
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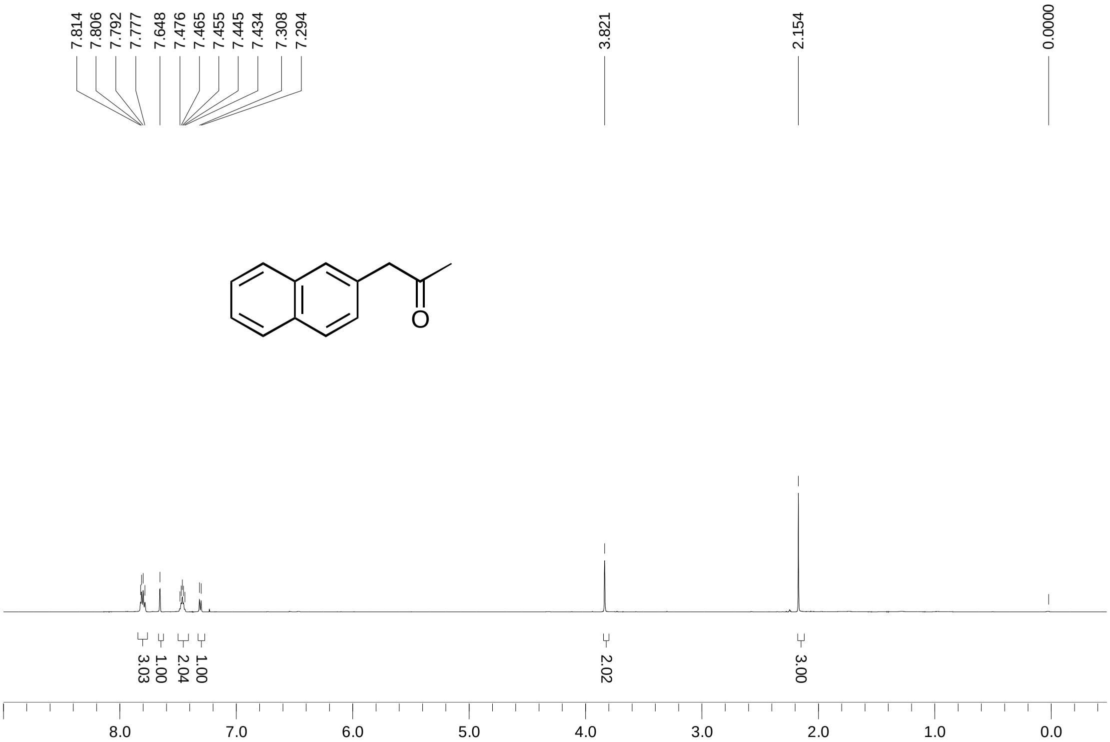
129.709
129.458
129.245
125.609
125.493
124.973
123.172
50.321
29.605
225
200
175
150
125
100
75
50
25
0
ppm (f1)

3m


7.814
7.806
7.792
7.777
7.648
7.476
7.465
7.455
7.445
7.434
7.308
7.294
3.821
2.154
0.0000
O
3.03
1.00
2.04
1.00
2.02
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

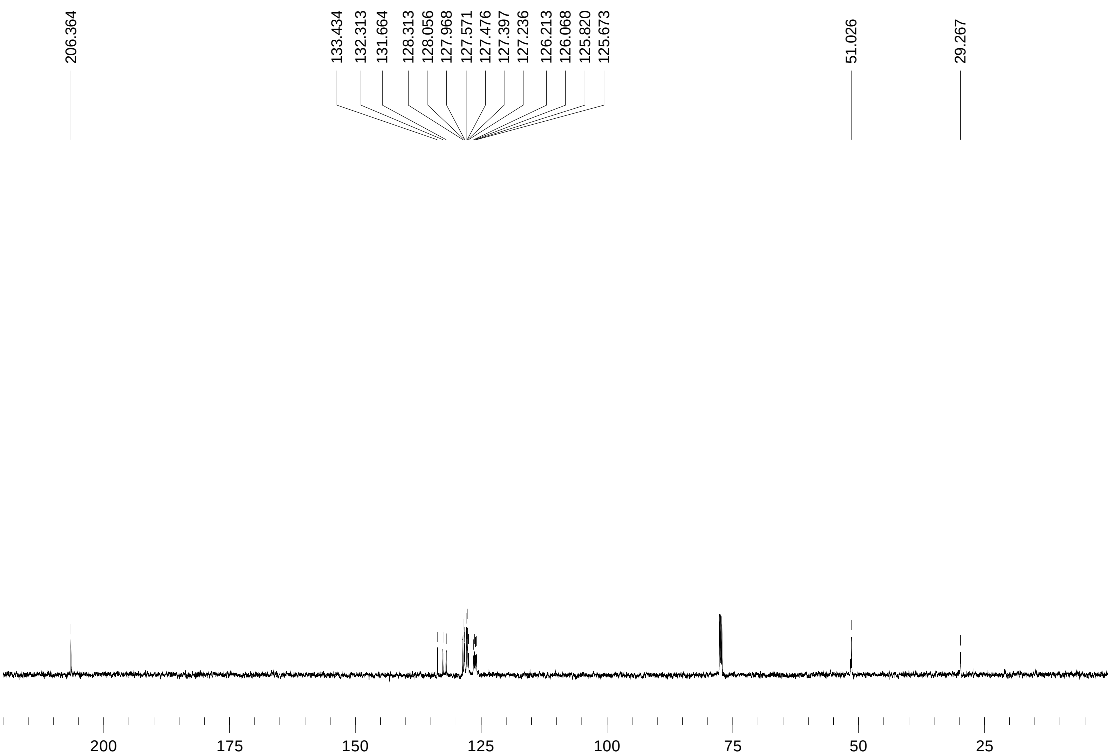

206.364
133.434
132.313
131.664
128.313
128.056
127.968
127.571
127.476
127.397
127.236
126.213
126.068
125.820
125.673
51.026
29.267
200
175
150
125
100
75
50
25

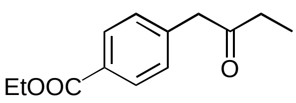
Table 4

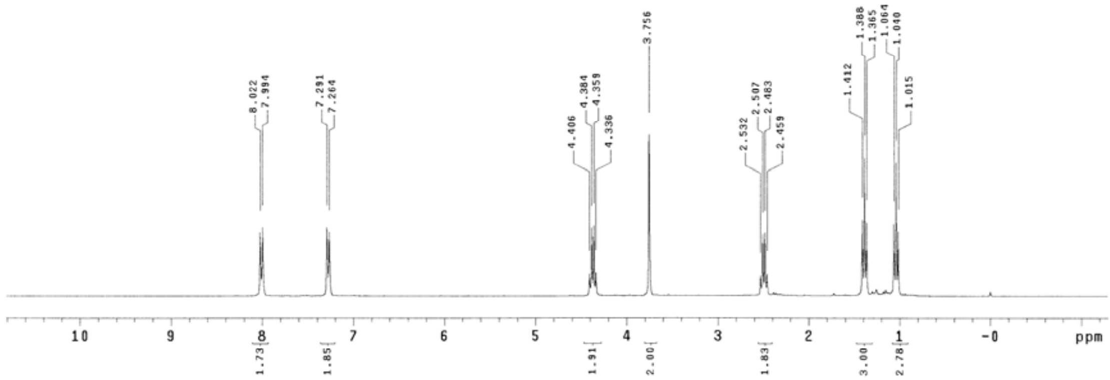
3n

hc-5-075-B

Archive directory: /export/home/wu/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul

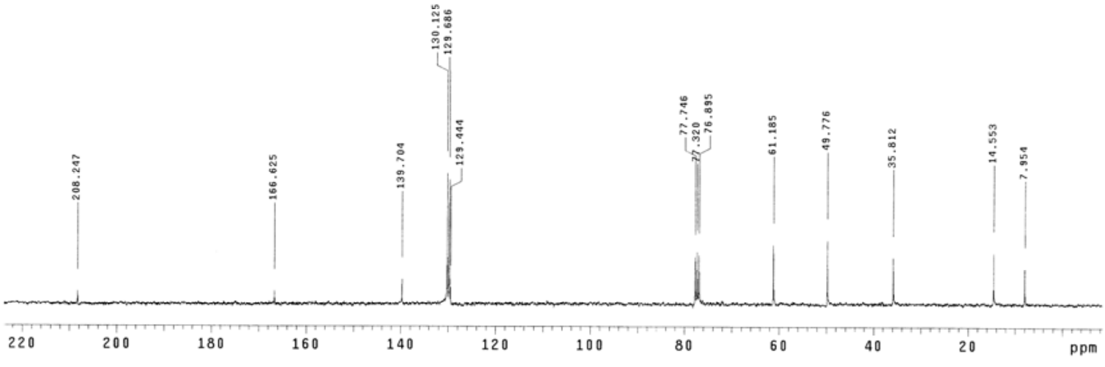




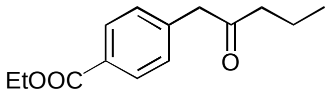
hc-5-075-B.c13

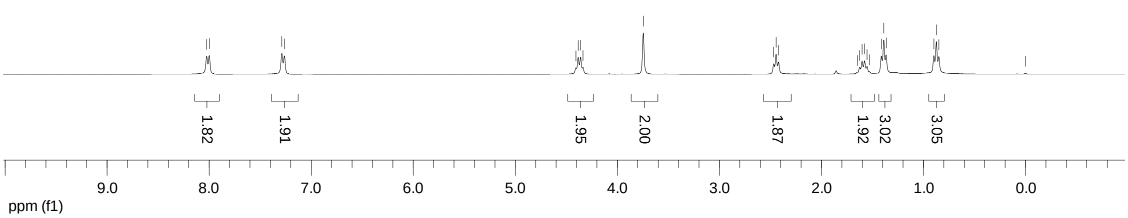
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

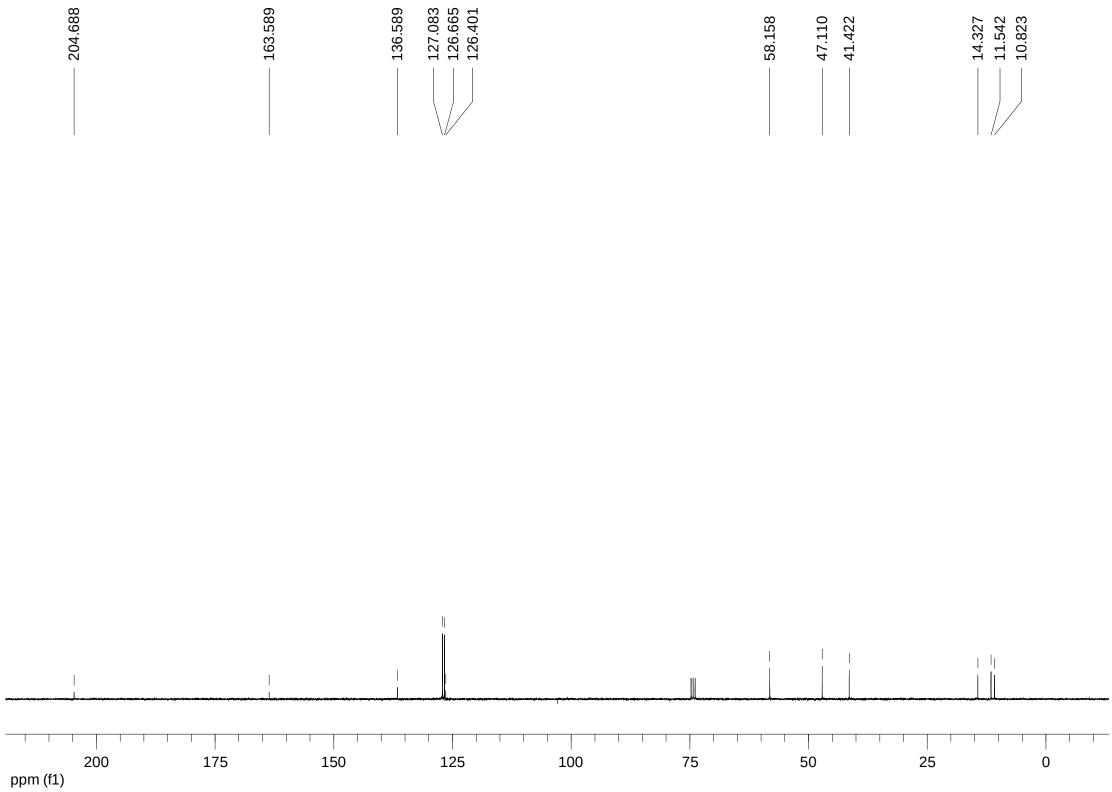
Relax. delay 1.000 sec
Pulse 28.0 degrees
Acq. time 0.500 sec
Width 17543.9 Hz
144 repetitions
OBSERVE C13, 75.4552576 MHz
DECOUPLE H1, 300.0819042 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 4.0 Hz
FT size 32768
Total time 2 hr, 24 min, 23 sec



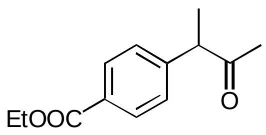
3o

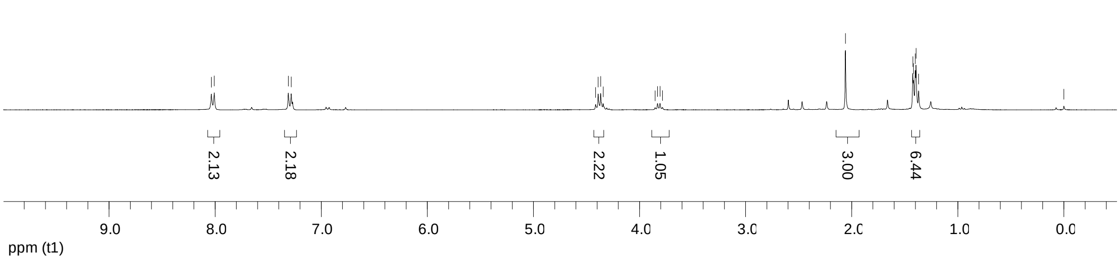

EtOOC
O

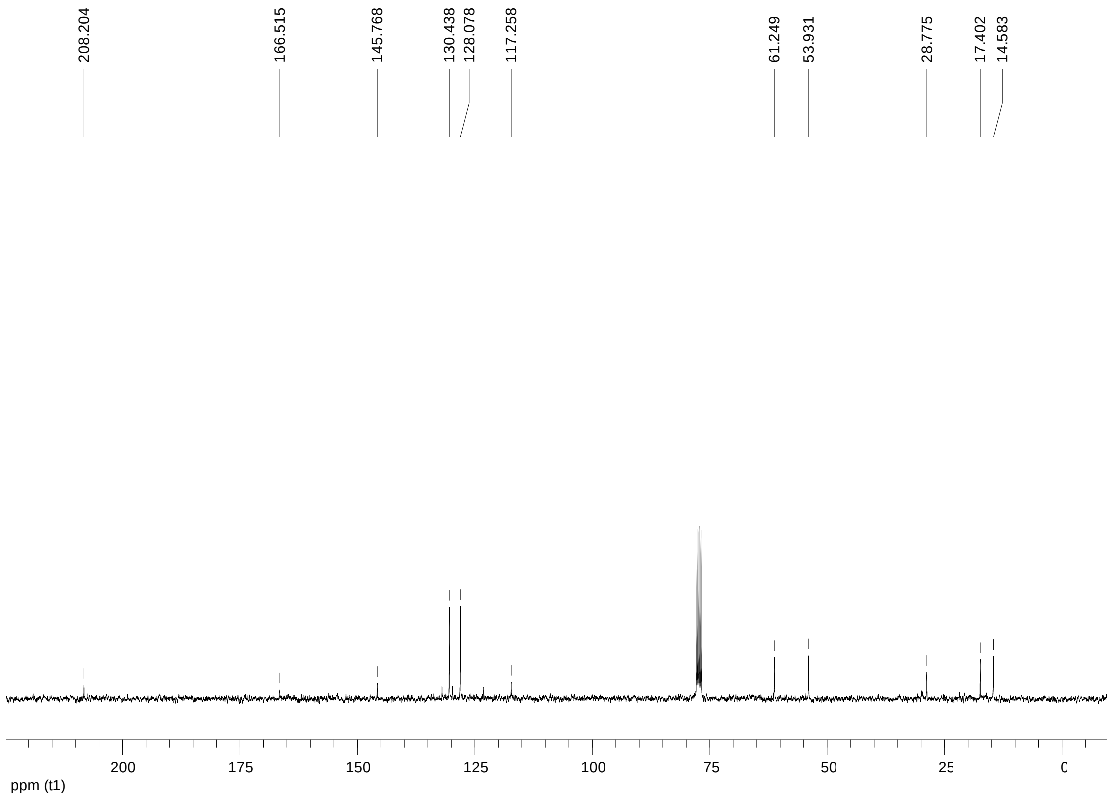

8.024
7.998
7.287
7.262
4.406
4.383
4.360
4.337
3.745
2.467
2.444
2.420
1.648
1.625
1.601
1.577
1.553
1.530
1.412
1.389
1.366
0.897
0.873
0.849
0.000000
1.82
1.91
1.95
2.00
1.87
1.92
3.02
3.05
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


204.688
163.589
136.589
127.083
126.665
126.401
58.158
47.110
41.422
14.327
11.542
10.823
200
175
150
125
100
75
50
25
0
ppm (f1)

3p

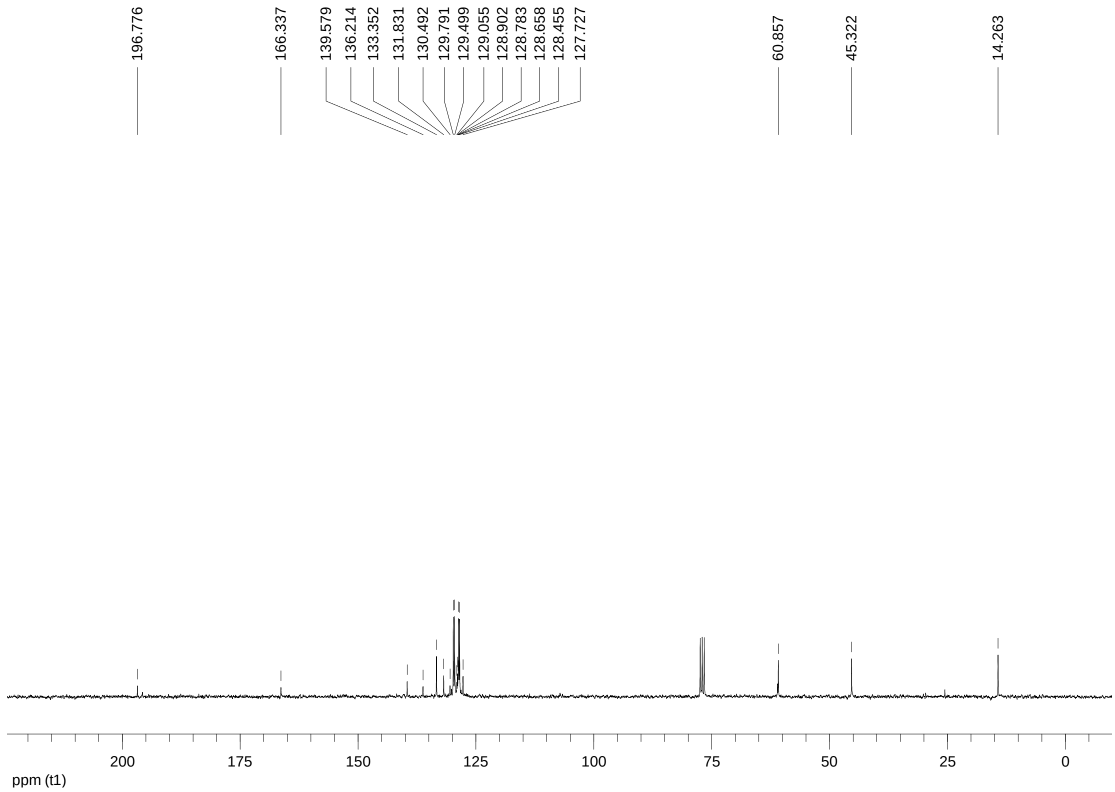

EtOOC
O


8.035
8.008
7.310
7.283
4.414
4.390
4.366
4.342
3.853
3.830
3.806
3.783
2.059
1.424
1.418
1.401
1.394
1.369
-0.000000
2.13
2.18
2.22
1.05
3.00
6.44
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


208.204
166.515
145.768
130.438
128.078
117.258
61.249
53.931
28.775
17.402
14.583
200
175
150
125
100
75
50
25
0
ppm (t1)

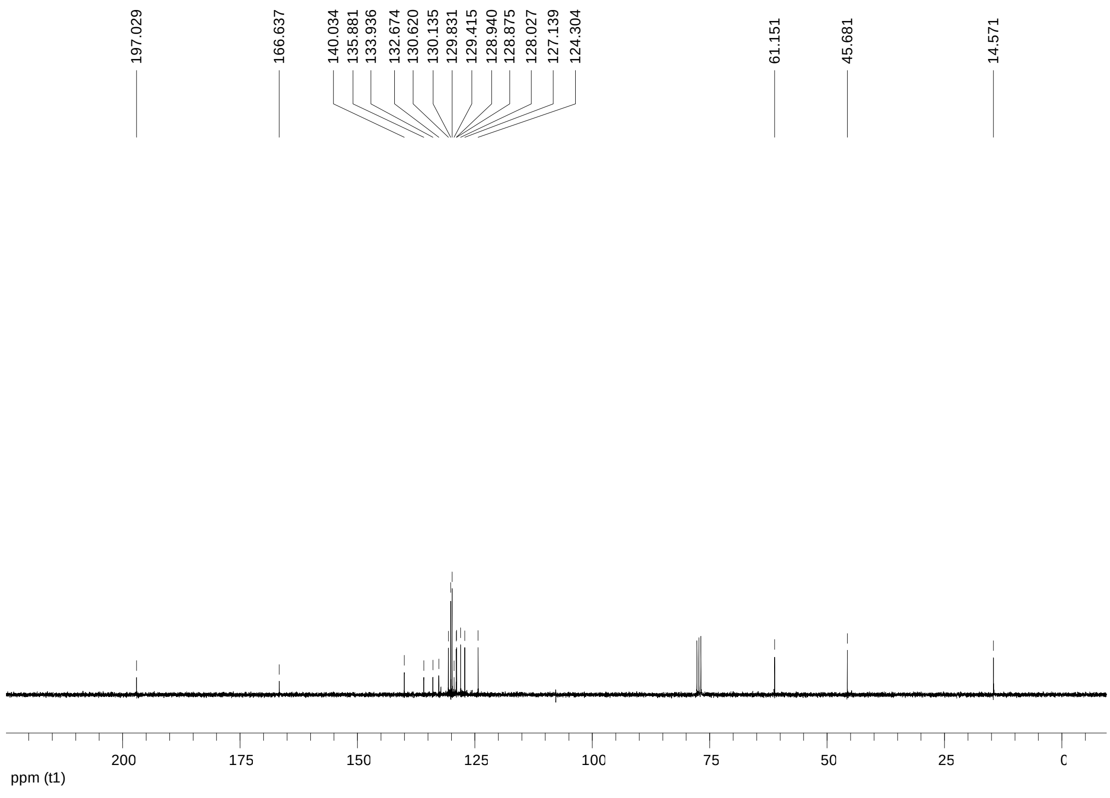
3q


EtOOC
O
8.027
8.020
8.000
7.993
7.598
7.574
7.549
7.491
7.465
7.441
7.351
7.323
7.232
7.210
7.184
7.177
7.152
4.396
4.382
4.372
4.348
4.325
1.400
1.376
1.353
-0.00000
3.11
0.89
1.86
1.65
1.04
3.96
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


196.776
166.337
139.579
136.214
133.352
131.831
130.492
129.791
129.499
129.055
128.902
128.783
128.658
128.455
127.727
60.857
45.322
14.263
200
175
150
125
100
75
50
25
0
ppm (t1)

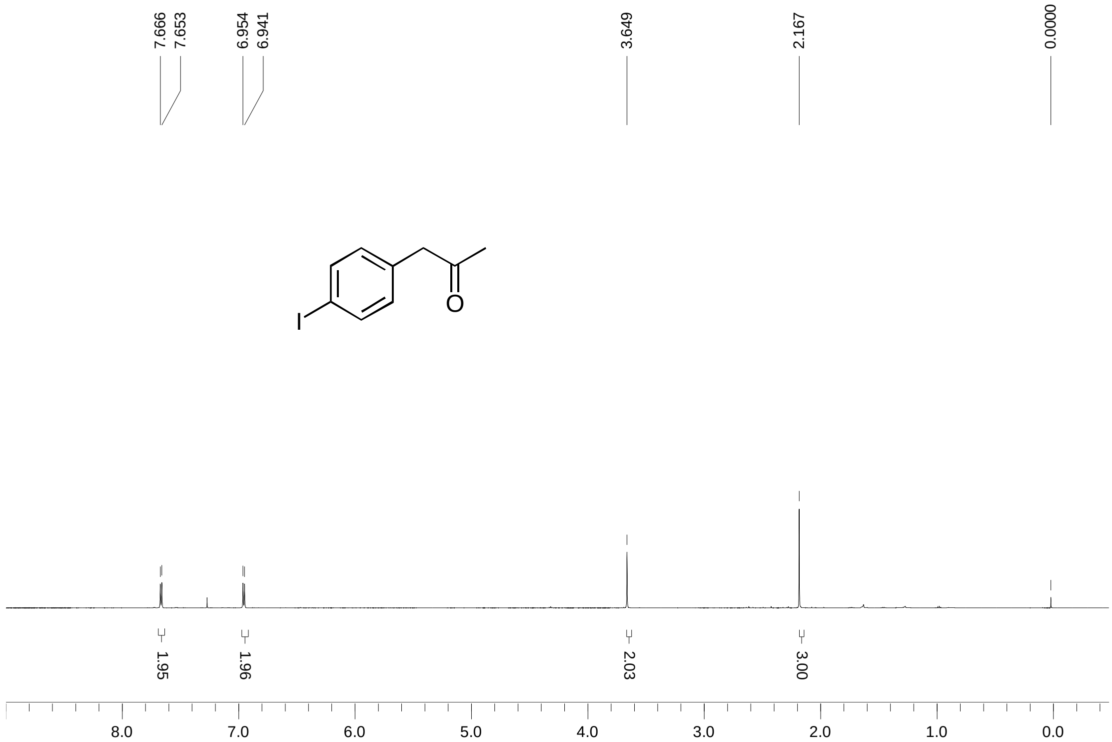
3r

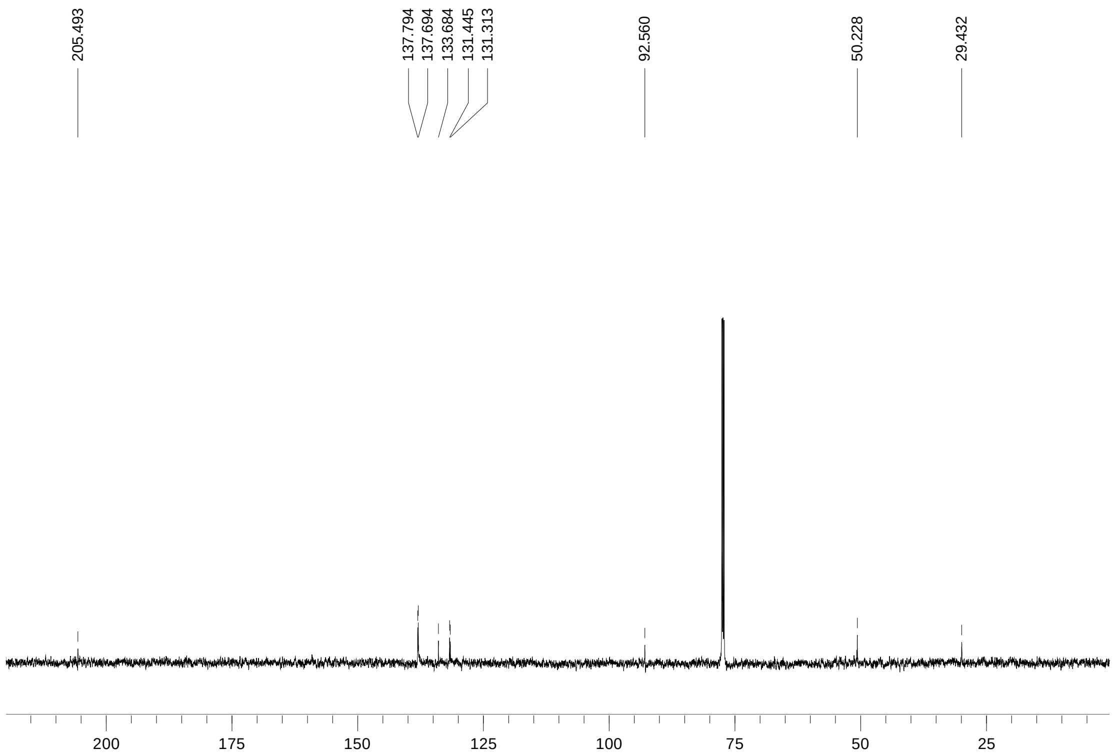

8.525
8.053
8.033
8.007
7.965
7.939
7.898
7.871
7.850
7.625
7.602
7.575
7.548
7.525
7.394
7.367
4.466
4.391
4.367
4.344
4.320
1.393
1.369
1.346
-0.000000
EtOOC
O
0.86
5.78
2.19
1.76
1.88
2.06
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


197.029
166.637
140.034
135.881
133.936
132.674
130.620
130.135
129.831
129.415
128.940
128.875
128.027
127.139
124.304
61.151
45.681
14.571
200
175
150
125
100
75
50
25
0
ppm (t1)

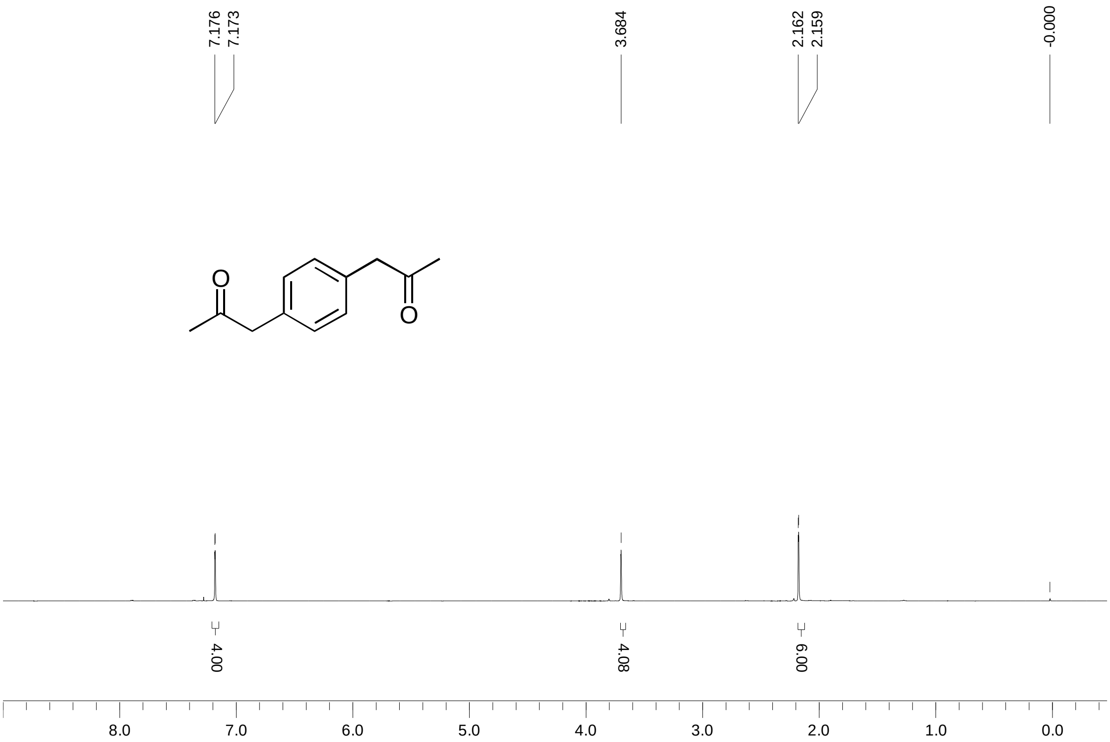
Equation 4

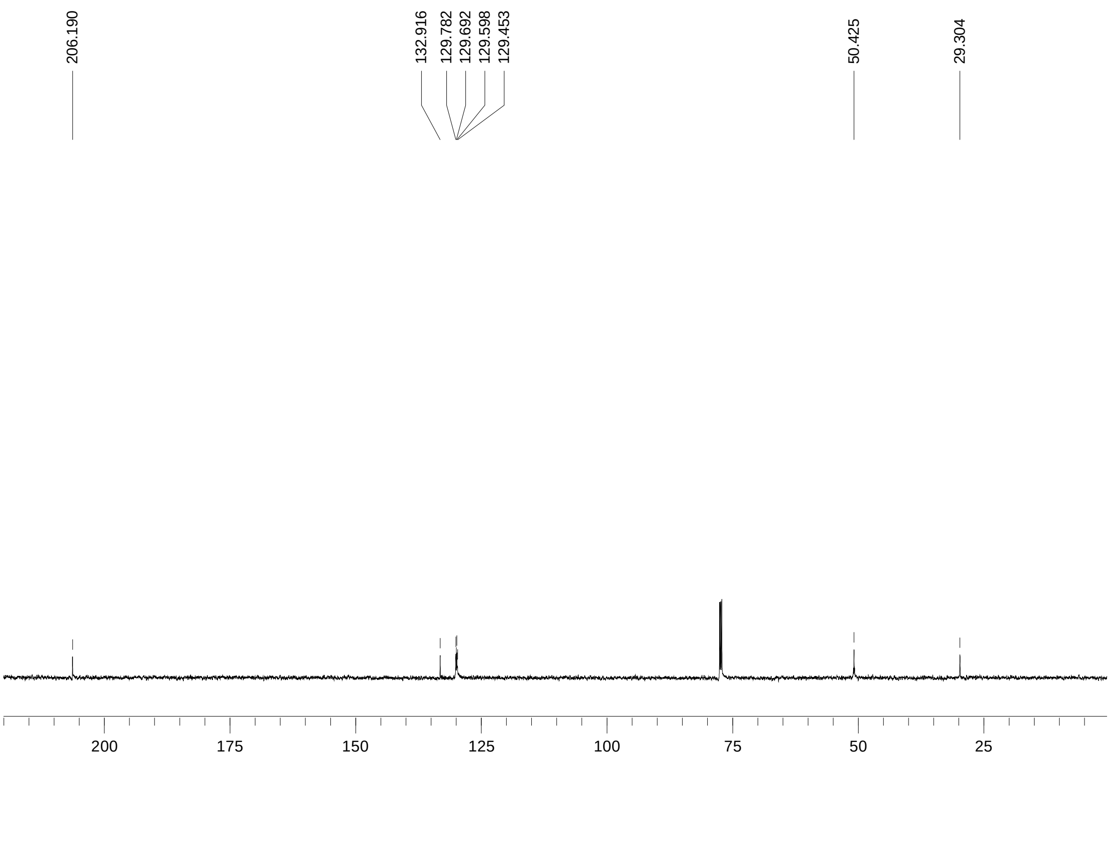
3t





3u


7.176
7.173
3.684
2.162
2.159
-0.000
O
O
4.00
4.08
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


206.190
132.916
129.782
129.692
129.598
129.453
50.425
29.304
200
175
150
125
100
75
50
25